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**THE CHEMISTRY OF
DENTAL MATERIALS**

THE CHEMISTRY OF DENTAL MATERIALS

BY

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PREFACE

The Chemistry of Dental Materials is largely based on notes of lectures delivered to dental students in the Chemical Department of Guy's Hospital Medical School. To describe adequately the origin and properties of the large and continually increasing number of materials available in dental practice would require a comprehensive dictionary, and I have therefore tried to describe representative materials so as to make the study of the book an introduction to the more specialised literature. Further, I have assumed on the part of the reader only such a knowledge of chemistry and physics as is covered by the syllabus of the Preliminary Scientific Examination for the Licentiate in Dental Surgery of the Royal College of Surgeons of England. As far as possible, I have tried to emphasise the practical applications of the materials described, and I hope the book will be found specially useful by the student during his professional training in Dental Mechanics. At the same time it may serve to emphasise not only to the dental student, but also to the dental surgeon the importance of obtaining as complete a knowledge as possible of the properties of materials which are, or may be, available to assist in perfecting the healing art of dentistry.

As far as possible, I have given references to the more comprehensive treatises and original papers on the subjects dealt with, and I desire to acknowledge information obtained from articles in the 1912 and the new edition of Sir T. E. Thorpe's *Dictionary of Applied Chemistry*, from Professor Desch's *Metallography*, from Dr Wilson's *Dental Prosthetics*, and from Landolt-Börnstein's *Physikalisch-Chemische Tabellen*.

Whatever merit the book may possess is due, in the main, to the great help and encouragement which I have received from Mr Montagu Hopson, L.D.S., Senior Dental Surgeon of Guy's Hospital. Mr Hopson placed in my hands the notes for a proposed book on a similar subject written by him in collaboration with the late Dr J. Wade, late Lecturer in Chemistry at Guy's Hospital Medical School. Mr Hopson and Dr Wade proposed to give their book the title *Dental Hylology*, and I desire to acknowledge the use I have freely made of the notes. It is

also difficult to express adequately my indebtedness to Mr W. Kelsey Fry, M.C., M.R.C.S., L.R.C.P., L.D.S., Assistant Dental Surgeon and Director of the Prosthetic Laboratory at Guy's Hospital. Mr Fry has not spared himself in offering suggestions and advice, and he also wrote the account of the uses of aluminium in dentistry.

I wish also to express my thanks to my predecessor, Professor T. Martin Lowry, C.B.E., F.R.S., of the University of Cambridge, and to Messrs Macmillan & Co. for allowing me to use the following illustrations taken from Lowry's *Inorganic Chemistry*: figs. 6, 9-12, 14-18, and 20-24. This work I have found particularly helpful in suggesting modes of presentation of certain parts of the subject.

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INTRODUCTION

SURVEY OF THE USE OF VARIOUS DENTAL MATERIALS

FROM the nature of his work it is obvious that to the dental surgeon an intimate knowledge of the chemical and physical properties of the materials at his disposal is as necessary as a close acquaintance with the more strictly medical sciences. Not only is the dental practitioner called upon to eliminate morbid conditions in the mouth and to correct irregularities, but, when necessary, he has to be prepared to restore or replace oral tissues. What are described as **conservative materials** are used for restoring a defective tooth to its original form and the protection of its sensitive tissues against further decay. **Prosthetic materials** are employed for the artificial replacement of lost teeth or other portions of the mouth when conservative treatment is no longer applicable. For the mechanical correction of irregularities, **orthodontic materials** are used, while in preparing and working the foregoing the dentist employs very diverse **laboratory materials**.

Amongst dental materials the metals occupy a leading position, and, what is generally known as "Dental Metallurgy," or the study of metals and alloys, including amalgams used in dentistry, has an important place in the training of the dentist; but, since various non-metallic substances are also largely employed in dental practice, it is proposed to include the study of some of these also in the present work.

Conservative and Filling Materials.—Since the primary cause of the caries of teeth is almost invariably the action of bacteria which have established themselves owing primarily to the disintegration of the otherwise impervious enamel of the teeth, the maintenance of aseptic conditions in the mouth is of primary importance in dental conservative work. Hence among conservative materials we have detergents and polishing powders, such as soap and chalk, as cleaning materials, and, in addition, antiseptics such as phenol, formalin, hydrogen peroxide, etc.

When, from whatever cause, caries has actually commenced, and it is therefore desirable to prevent further decay, the degraded portion of the tooth must be mechanically removed by means of various instruments, excavators, burrs, etc., which are made of steel. After the degraded enamel and dentine have been removed, the cavity requires careful sterilisation by means of a suitable antiseptic, such as phenol, before being filled by appropriate material to replace the degraded natural tissue which has been removed. The filling material is introduced by plugger points made of steel, ground on discs of carborundum, and finally polished by pumice or whitening.

The ideal filling material would possess the following properties :— It would be introduced easily and adhere firmly to the cavity walls, and when once in position would neither expand, contract, nor warp. It would not be affected by oral fluids, and would have no deleterious chemical action on the hard and soft tissues in the mouth. It would be a non-conductor of thermal changes, would match the tooth in colour and appearance, and by being capable of taking and maintaining a high polish, would not form a nidus for bacteria and food debris.

No single material at the disposal of the dental surgeon possesses all these properties, and, accordingly he selects from those available the particular material which he deems most suitable for the particular purpose.

Among filling materials the various forms of pure **gold** have long and do still occupy a prominent place. Pure gold possesses the property of being welded in the cold, it preserves its form, and when properly manipulated forms a perfectly water-tight plug. Further, it can be built out to represent the original tooth, it maintains its colour, is chemically inert under general oral conditions, and retains its high polish, leaving no surface to which fermentable food can adhere. On the other hand, a gold filling can only be applied to a tooth of fairly strong structure, and the walls must be capable of withstanding the strain involved in condensing it. The tooth, again, must be easily accessible, and capable of being kept perfectly dry during filling. Further disadvantages attached to the use of gold as a filling material are due to its being an excellent conductor of thermal changes, and to its pronounced colour, which harmonises badly with the natural colour of the tooth. To obviate these disadvantages to some extent, other pure metals, such as **tin** and **platinum** may be alloyed with the gold in small quantities.

Amalgams, alloys of mercury with other metals, are, next to gold, the most important and most generally useful filling materials. The majority of amalgams for filling purposes are made up, starting with the **silver-tin** alloy as the chief constituent. The amalgams are easily introduced, and make a tight filling. They are, however, liable to change of form, and generally undergo at least superficial chemical change in the mouth. Like gold, but not to the same extent, they are good conductors of heat, and they are also liable to dissolve the tooth substance.

For fillings of a more or less temporary nature, the so-called "**osteo-cements**" are of very great service. The most important of these are certain basic salts of zinc, viz., the oxychloride, oxysulphate, and oxyphosphate, and basic aluminium silicates. These cements set in a similar manner to builders' cements, but more rapidly and durably. The cements, when set, form hard solids, which are poor conductors of thermal changes, and, especially in the case of the

silicates, approximate closely to the natural colour of the tooth. They adhere so firmly to the walls of the cavity that they actually strengthen them, and so permit conservative treatment in cases where it would not be otherwise possible. The chief disadvantage attached to their use arises from a certain irritant action which they have on the dental pulp. This may be due to a slow hydrolytic action which goes on under the conditions in the mouth and whereby the cements become gradually undermined. The zinc cements find a very important use in lining cavities for metallic fillings, and as fixing agents for crowns and regulating appliances.

Porcelain, in the form of an inlay, probably approaches most nearly to the ideal tooth-filling material. The ground inlay is shaped to the cavity by grinding, while the fused inlay, which has now largely replaced the ground variety, is made for the cavity by fusing it in a suitable furnace to a gold or platinum matrix previously made to conform to the cavity. Porcelain undoubtedly possesses great advantages as a filling material. It is hard and incorrodible, it can be moulded to any form, and coloured almost indistinguishably from the tooth. It is, however, somewhat brittle, and dependent on the osteo-cement, with which the cavity is lined, for its anchorage.

Although it is too soft for a permanent filling, **gutta-percha** is invaluable as a temporary substitute. It is easily introduced, and is the best non-conductor of thermal changes. Apart from its use as a temporary filling material in the ordinary way, gutta-percha is also employed as a root filling.

It often happens that a tooth has become so defective that conservative treatment is useless, and in these circumstances the defective tooth has to be replaced wholly or in part by an artificial substitute or **prosthetic**. **Prosthetic materials** fall into two classes, viz., artificial teeth which replace and fulfil the function of natural teeth, and their supports which also replace such portions of the jaw and palate lost by resorption and damage.

The ideal material for artificial teeth should be capable of being moulded or cut to any form; it should be hard, resistant to wear and to chemical action. For reasons of cleanliness, it should be capable of being highly polished, as in the case of fillings, and capable of being coloured to match any neighbouring natural teeth. As it has to be attached by metallic supports, it should be able to stand the temperature required in hard soldering.

The material which possesses these properties in almost every particular is porcelain, which therefore finds extensive use in prosthetic dentistry.

There are four varieties of porcelain teeth in common use, viz., **flat pin teeth**, **vulcanite pin teeth**, **diatoric teeth**, and **tube teeth**. Flat pin teeth and vulcanite pin teeth are provided with small pins of **platinum**, which project from the posterior surface of the teeth in a

horizontal direction, the heads being fused into the porcelain. Diatoric teeth, which are fixed by vulcanisation, are, as the name implies, provided with pierced or counter-sunk holes, into which the plastic caoutchouc flows during the process of vulcanisation. Tube teeth are furnished with a central vertical tube of platinum, which is exactly fitted by a **gold** pin soldered to the plate. The tooth is cemented to this pin by melting **sulphur** round it, so as to fill completely the minute space between the pin and the platinum tube.

The artificial teeth are in most cases mounted on plates which can be removed from the mouth. These plates also to a certain extent replace deficiencies in the jaw or palate. Since the plates are worn more or less permanently in the mouth, it is essential that the material of which they are made should resist chemical action. It must be hard and tough in order that it may be thin, and therefore take up as little room as possible. It must possess such properties as make it capable of being worked to the contour of the palate. It must allow of artificial teeth and their attachment pins being fixed to it by suitable means. It is desirable that it should be a poor conductor of heat, and of a high specific heat to minimise thermal changes, impermeable to fluids, and devoid of irritant action on the oral tissues.

Although pure gold is too soft for use as a dental base, when alloyed with small quantities of other metals, such as **copper**, **silver**, and **platinum**, so as to produce gold of 18 to 20 carat, it is very largely used. The small proportion of other metals imparts the necessary rigidity without greatly impairing its tenacity and malleability. Further, gold of this quality is still practically incorrodible in the mouth, but owing to its high conductivity and low specific heat, it conducts thermal changes too rapidly.

Dental alloy, containing silver and platinum, and the alloy containing silver and **palladium**, may be used as a substitute for 18 to 20 carat gold. They have a higher melting-point, but tarnish in the mouth, and are more difficult to work than 18 to 20 carat gold.

The lightness of **aluminium**, its low conductivity and fairly high specific heat are qualities which few other metals possess, and which recommend its use as a dental base material. This metal has not found extensive use so far, probably owing to the fact that the commercial metal available up to the present undergoes somewhat rapid corrosion in some mouths, and because no thoroughly satisfactory solder for aluminium has been found. The ease with which aluminium castings can be made, however, may, now that aluminium of high degree of purity is available, bring this metal into extensive use for the making of cast dental plates.

The alloy of aluminium (10 to 5 per cent.) with copper (90 to 95 per cent.), known as **aluminium bronze**, has found considerable use in other countries as a material for making swaged dental plates.

This alloy, which resembles gold in appearance, is the strongest of all the copper alloys. It is stated to oxidise but superficially in the mouth.

Certain alloys which fuse easily and run well when molten are also used for making denture plates, which are simply cast in the ordinary manner. Such alloys as Weston's and Gartrell's comply with these conditions, giving fairly strong castings. These alloys melt at about 200° C., and contain *tin* as the chief constituent metal.

Vulcanite, a somewhat indefinite compound of caoutchouc and sulphur, is the material most frequently employed in the making of denture bases. Being made to conform to the plaster model of the mouth whilst still plastic, it can be made to produce an exact fit. It is moderately strong, and owing to its non-conducting properties it conducts thermal changes with great slowness. On the other hand, it is bulky in the mouth, difficult to keep clean, and occasionally irritating to the oral membranes.

For the making of temporary dentures, **celluloid** is employed. Celluloid is a colloid composed of nitrocellulose (pyroxylin) and camphor, which can be rendered opaque with zinc oxide, and tinted to resemble the colour of the mouth with **vermilion** (mercuric sulphide). Owing to its plasticity, especially when still containing part of its volatile solvents, and the ease with which it is welded in this condition, it can be moulded to the exact contour of the mouth like vulcanite. Celluloid is light and strong, but the drawbacks with which its use is attended are due to its inflammable nature, and to its having a distinct taste of camphor.

When the artificial teeth have to be fused to one another and to the plate by coloured porcelain, as in continuous-gum work, the material of the base must melt at a higher temperature than the porcelain, it must expand at nearly the same rate to avoid cracking on cooling, and it must not be acted upon chemically by the oral fluids. Platinum is the material which is used in this connection, as it is the only substance which fulfils these conditions.

When it is possible to attach an artificial crown to a natural tooth root, the crown, if visible, is made of porcelain, and attached by means of suitable metallic materials. If the crown is attached to a molar tooth root, it may be made entirely of metal. Several crowns may be connected by a metallic bridge, which is fixed to the crowns at the ends of the assemblage.

A denture which replaces only a portion of the natural teeth and attendant tissues is retained in position in the mouth by means of small metallic bands or clasps which partly encircle two or more of the existing teeth. These bands or clasps must possess a certain springiness, and the materials of which they are made must conform to the conditions already described with regard to the properties of metallic materials in the mouth. Gold, alloyed with a small amount of

platinum, is used for making such bands or clasps. When the mouth is edentulous, or devoid of natural teeth, and the alveolar ridges have been lost by absorption, small spiral springs have sometimes to be employed to keep the plates in position. These springs are attached, one on either side, to both dentures, and are made either of the springy gold-platinum alloy, silver gilt, or of German silver (alloy of copper, zinc and nickel) gilt.

Orthodontic materials are those of which appliances are made for the correction of irregularities in the position and occlusion of the teeth. These appliances consist essentially of elements of power, viz., the lever, screw, and inclined plane, supplemented by certain elastic substances. These appliances are mounted on removable plates similar to those used for prosthetic purposes, or attached to thin metal bands, which accurately fit and are cemented to the crowns of selected natural teeth.

Orthodontic appliances having to be worn in the mouth, the materials of which they are made will be for the most part the same as those for prosthetic purposes. The fact that such appliances are worn in the mouth for a comparatively short time makes it possible to use also less chemically resistant materials, *e.g.* **brass** (alloy of copper and zinc), **German silver**, various kinds of **steel**, and **rubber**.

Dental splints for the treatment of jaw fracture may be made of vulcanite and of metal. When some portion of the soft palate is lacking, as in congenital cleft palate, or as a result of injury or disease, a modified form of dental plate, known as an obturator, may be supplied, constructed from prosthetic materials. In order to impart the necessary resiliency to the part supplying the soft palate deficiency, a special form of vulcanised rubber, known as **velum rubber**, is employed.

The making of the various prosthetic and orthodontic appliances makes it necessary for the dentist to be able to use a considerable number of what may, for our purpose, be called **laboratory materials**. The prosthetic or orthodontic appliances are fashioned according to a model of the mouth made as accurately as possible.

The model of the mouth is almost invariably made by casting from an impression taken from the mouth. The material of which the impression is made should be capable of being introduced into the mouth in so plastic a state as to distort the softer tissues as little as possible. When once in place it should harden rapidly, and yet be capable of being removed from the mouth easily and from all undercut without damage; further, it should neither expand nor contract on setting. The material which has been found most satisfactory for the purpose is **plaster of Paris**, which is partly dehydrated crystalline calcium sulphate, and which has the chemical composition $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. To assist its more rapid setting, the plaster of Paris (2 parts) is mixed with a 7 per cent. aqueous solution of alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (1 part) instead

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of with water. Plaster of Paris gives a perfect impression without displacing the soft tissues. Although it cannot generally be removed from undercuts without fracture, this drawback is not a serious one, since the broken parts can be fastened together, subsequent to removal from the mouth, with great accuracy. Plaster of Paris expands slightly on setting, but the expansion can be reduced by suitable means (page 137).

Other impression material employed is known as **dental composition**, which is a somewhat indefinite, but intimate, mixture of beeswax, stearine, and French chalk with suitable colouring material. This composition is easily manipulated when softened at a temperature which can be tolerated in the mouth, and contracts but slightly on cooling. It is inelastic, and therefore liable to distortion on removal, and the force necessary to adapt it to the palate displaces the softer tissues. Gutta-percha is also employed as an impression material.

The impression material is supported by an impression tray, the material of which must be sufficiently rigid to withstand pressure without yielding. Impression trays are generally made of German silver, which suits the purpose admirably. When stock impression trays cannot be used, as, for example, when the mouth is irregular, or the teeth sparse or malplaced, special trays are required to suit particular cases to ensure uniform distribution of the impression material. Such trays may be made either by swaging German silver sheet, or by casting either tin or **Britannia metal**, an alloy of tin, antimony, copper, and lead.

From the impression taken from the mouth, the model of the mouth is made of the material most suitable for the purpose, viz., plaster of Paris. The reduction of the expansion which ordinary plaster of Paris undergoes on setting may be largely minimised by using a mixture consisting of 1 part **Portland cement** with 2 parts of plaster of Paris. When mixed with water, it is so fluid as to follow accurately every detail of the impression, and yet it sets rapidly to a hard and fairly strong solid. The plaster impression is easily removed from the model if the former has previously been thoroughly moistened with soap solution applied with a soft brush. If a beeswax composition material has been used as the impression material, this again is easily removed from the plaster model by immersing in hot water so as to soften the impression material sufficiently to be peeled off easily.

In order to ascertain the natural relation of the jaws, and secure the proper articulation and occlusion of the artificial teeth, bite plates are employed. These are dummy denture plates furnished with ridges of soft wax to receive the indentations from the remaining natural teeth when the jaws are in correct contact. Bite plates are made of some easily mouldable material, such as gutta-percha or soft metal, or the metal denture itself may be utilised before the teeth are

attached. The correct articulation having been secured, the artificial teeth can be set up on the model by imbedding them, together with any necessary bands or clasps, in wax.

The permanent base or plate supporting the artificial teeth or orthodontic appliance is made, as has been pointed out, either of metal, vulcanite, or celluloid. A metal plate may be either swaged or cast, and for the making of a swaged plate metallic dies or moulds are necessary, while for a cast metal or for a vulcanite plate, or one made of celluloid, a plaster mould is necessary. Such dies or moulds are necessarily produced, or inverted, from the plaster model. Dies are models of the mouth, and in casting them a secondary intermediary mould is necessary. This is made of **sand** taken directly from the plaster model, which, for this purpose, must be hardened by immersion in melted stearine or by coating with varnish.

The ideal material for a **dental die** should melt at a moderate temperature, should not contract during solidification, and run freely when molten. It would be so hard and tough as to avoid any possibility of injury during the swaging or beating of the sheet metal into shape. For such a purpose, a metallic material is the only possible one, and **zinc** is the metal most frequently employed. Zinc, however, contracts considerably on cooling, and therefore various alloys have been proposed for the same purpose. The alloys most frequently employed are **tin-zinc** alloy, **type metal** (lead-antimony-tin alloy), **Babbitt's metal** (copper-antimony-tin alloy), and a fusible mixture of ferrous sulphide and sulphur, known as **Spence's "Metal."**

The **counter-die**, against which the plate material is forced during swaging, and which is a reproduction of the original impression, is cast from the die. If the melting-point of the counter-die material is close to that of the material of which the die is made, the latter can be protected by a coating of graphite or plumbago while the casting of the counter-die is being made. The counter-die material should be somewhat softer than the material of the die, so that it may yield slightly to the metal plate as this is forced into shape. **Lead** and **tin** are the metals most commonly used, especially in completing the swaging of a gold or a dental alloy (silver-platinum alloy) plate.

For the making of a swaged metal plate, it is first necessary to cut the metal approximately to size from a plate pattern, obtained by pressing thin **lead** foil on the die, and trimming the foil to shape. The lead foil pattern can then be opened out and the metal sheet cut roughly to it, and worked into the die by beating with a mallet made of **horn** or similarly hard springy material. The swaging or final shaping is then effected by hammering on the die against the counter-die. Frequent annealing or heating, followed by slow cooling of the plate, is necessary during the process to counteract the immediate effects of the swaging, whereby the metal tends to become hard and springy, and its malleability considerably diminished. When the swaging is complete the

surplus metal is trimmed away by suitable instruments, and especially in the case of a gold plate, since the smallest trace of lead or zinc renders it brittle, care must be taken to remove any such contamination derived from the die or counter-die. A gold plate is easily freed from such impurities by the process technically known as "pickling," that is, immersion in dilute nitric acid. The necessary bands or clasps are shaped and fitted to the natural teeth, as represented on the plaster model, for which purpose suitable tools such as pliers, shears, and files made of steel are necessary. The bands made of the springy gold-platinum alloy are then soldered to the plate.

The selected porcelain teeth having been ground on the carborundum wheel so as to fit exactly that portion of the plaster model which represents the gum, and their occlusion with opposing teeth having been secured in a similar manner, are ready for fixing to the plate. Flat pin teeth are fixed to the swaged denture by soldering. The teeth are first temporarily fixed to the denture by means of wax, and the whole is invested in a suitable plaster mixture. This plaster mixture has to stand the high temperature of soldering without cracking, and hence the plaster of Paris is mixed with asbestos powder and sand. It is necessary to leave those parts of the teeth and plate which have to be soldered free from plaster. When the investment has set, the wax is removed by means of boiling water. The teeth, firmly held in position, are now ready for fastening to the plate.

The fastening material employed must obviously have the same resisting power to the oral fluids as the metal of the plate itself, and it must not have any chemical action on the tooth or plate material. It must melt at a considerably lower temperature than these. With backed teeth, a permanent and strong connection between the metal and the plate backing can only be made by means of a metallic solder. This solder must consist largely of gold in order to resist the action of the oral fluids. The necessary lowering of the melting-point of the gold is secured by alloying with it **silver** and a little **copper** and **zinc**. The addition of these metals to gold, within certain limits, does not materially affect the chemical-resisting properties of the gold for dental purposes. Such a solder is termed a **hard solder** for the reasons that it is mechanically hard and can only be fused at the temperature of the blow-pipe.

The metallic surfaces which have to be soldered together are cleaned in the usual way with **borax** or similar flux, and the solder applied in small strips or in the form of filings and melted by means of a suitable blowpipe, and in this manner the teeth are fixed in the required position to the plate. What is known as **soft solder** (alloys of tin and lead in various proportions) could not be used in such circumstances. It would be oxidised at the temperature of soldering, and, apart from that, would possess other undesirable properties in the mouth. The plate with its teeth is now freed from plaster, excess of

solder trimmed away by means of suitable steel tools, and finally polished by means of polishing materials of suitable degrees of hardness.

The fixing of vulcanite pin teeth and diatoric teeth to a swaged metal plate is carried out in much the same way as the construction of a vulcanite plate (see below). The teeth are fixed temporarily to the metal plate by means of wax, and the whole embedded in plaster. The wax is replaced by means of soft rubber, which is vulcanised in the ordinary manner.

In the construction of dentures of **vulcanite** and **celluloid**, dies are not required, whilst solders are only required in the fixing of bands and clasps. The teeth are fitted as before to the plaster model of the mouth by means of wax, which latter is also shaped to the model in every way to resemble the finished vulcanite plate, thus forming a temporary plate. Any bands or clasps are soldered to metal tags, which are also imbedded in the wax in their proper position. What may be termed the counter mould is made of ordinary plaster of Paris in the **gun metal** (copper alloyed with 8 to 10 per cent. of tin) vulcanising flask. The plaster model carrying the wax plate is imbedded in the plaster of the lower half of the vulcanising flask, so as to leave only the wax model of the palatal section uncovered. The exposed surface of the plaster is coated as usual with soap solution as soon as it has hardened, to prevent the adhesion of the next layer of plaster. The upper section of the flask having also been filled with plaster which is allowed to harden before the flask is closed and clamped.

The second lot of plaster having set, the flask is heated and then opened. A double plaster model is thus obtained, having the teeth in the exact position, and a vacant space corresponding exactly with that which is to be occupied by the vulcanite in the finished plate. The **rubber** used is specially prepared from pure rubber by thoroughly admixing it with sulphur and either **zinc oxide** or mercuric sulphide (vermilion), or both, in the cold. This prepared rubber, softened by warming at the temperature of a boiling-water bath, is carefully packed into the matrix of the model. The two parts of the flask are then clamped together, and the whole heated in the vulcaniser to a temperature of about 157° C. (315° F.). This temperature is attained by heating the water in the vulcaniser under pressure; the pressure registered at this temperature is approximately 90 lbs. to the square inch. It should be remembered that the conversion of the prepared rubber into vulcanite is only a matter of temperature, since the vulcanisation can be carried out at ordinary pressure, provided the above-mentioned temperature is maintained. The time of vulcanisation is approximately one and a quarter hours. Under these conditions the soft pliable rubber has become converted by a complex chemical change into a hard, tough, and elastic substance known as **vulcanite**, and is said to have been vulcanised. After cooling, the flask

is opened, and the plate, to which the teeth are now firmly attached by means of the pins or diatoric apertures, is removed from the plaster matrix and, after cleaning, filing and polishing, is ready for use.

The making of a celluloid denture involves processes very similar to those employed in the making of a vulcanite plate. The wax model of the plate, with the teeth and clasps in the correct position, is set up as before, and the investment of this in a flask containing investment material carried out in practically the same way. Celluloid is much less plastic than rubber when exposed to heat, and therefore much greater pressure is required to mould it to the surface of the model. Hence the flask is so arranged that its parts can be slowly screwed together as the temperature is raised, and the material gradually worked into shape by steadily increasing pressure. So great is the pressure employed that special precautions must be taken to produce moulds strong enough to resist fracture. In some cases moulds of tin or Babbitt's metal are advisable, or a tin face may be given to the plaster mould.

The mould having been prepared, celluloid sheet, shaped approximately to the model and slightly larger than that required for the finished plate, is softened in hot water and adapted as closely as possible to the surface of the mould, which has also been previously heated. The flask is now placed in a gas-heated chamber, and when the temperature reaches 107° C. (225° F.) pressure is brought to bear by slightly screwing down the still partly separated halves of the flask. As the temperature rises and the celluloid becomes more plastic, the halves are gradually screwed together tightly. The temperature is allowed to rise finally to 135° C. (275° F.), and as soon as the halves of the flask are tightly screwed together, the flask is removed from the heater and allowed to cool. The plate is then removed, cleaned, and trimmed.

The actual technique in making **cast-metal dentures** differs according to the nature of the metal used for the casting. Cast-metal dentures may be of **gold alloyed with small quantities of silver, copper, platinum, and palladium**. Pure gold is not suitable for making any part of a denture; it is not sufficiently hard and rigid. Silver is used chiefly to modify the colour, copper is used to give hardness and elasticity and to raise the melting-point; whilst palladium has the same purpose as the platinum, but has the advantage in that it unites more uniformly with the gold, and raises the melting-point more than platinum does, but it destroys the colour of the gold more than the latter metal. As for hard soldering, the investment material is plaster mixture, since ordinary plaster of Paris is not hard enough, and will not stand the necessary temperature without warping and cracking.

The technique in making a cast **aluminium** denture differs in many respects from that used in making one of gold alloy. The physical and chemical properties render these differences necessary, and plaster

mixture is again used as the investment material. Up to comparatively recently it was deemed impossible to make cast dentures with pure aluminium, and up to about the year 1907 various alloys of aluminium containing platinum, silver, and copper or tin were employed.

Various alloys of **tin** are also used for the making of cast-metal dentures. The alloys contain such metals as **bismuth**, silver, gold, and occasionally **cadmium** and **antimony**. These alloys of tin have low melting-points, and require similar investment material as for aluminium castings. It appears, however, more than likely that since aluminium can now be obtained so cheaply and of such a high degree of purity, and with the better understanding of successful aluminium casting, the use of the less cleanly and less durable tin alloys will gradually diminish.

The above rough survey of the more outstanding details of dental practice will serve to indicate the varied nature of the materials which the dentist has to use. The materials mentioned, however, by no means exhaust those generally at his disposal, since, especially in prosthetic work, many other substances, for example, most of the commoner metals, find at least occasional use in the dental laboratory.

In a general way the materials used in dentistry may be classified as follows :—

- (1) Metallic materials.
 - (a) "Noble" metals and their alloys.
 - (b) "Base" metals and their alloys.
 - (c) Mercury and the amalgams.
 - (d) Tool metals.
- (2) Non-metallic inorganic materials.
- (3) Organic materials.

It will be realised that metals constitute the largest possible class of the substances used in dental practice. The division of the chemical elements into two classes, non-metals and metals, is one of convenience for classification, and does not admit of exact definition. While it is possible in many cases to describe a particular element as non-metallic or metallic, there are individual cases where it is difficult to decide to which class a particular element should be assigned. Nevertheless, the metals, as a class, possess certain generic properties which the non-metals either do not possess at all or only in a very slight degree. Of the eighty-three elements known to chemists, by far the greater proportion, some sixty-three, possess in a greater or less degree the generic properties which allow them to be classed as metals. Only about one-third of the known metals find industrial application at the present time.

The metals, gold, silver, copper, iron, tin, and lead were known in very early times; references to them are found in New Testament writings. Certain metals, such as gold and silver, were early dis-

tinguished as "Noble" because they did not undergo any change in the furnace, in contradistinction to bastard or "Base" metals, which suffered change (oxidation) when heated in air. Nowadays, we regard those metals as noble which possess the negative property of chemical inertness under conditions when the base metals would undergo more or less rapid change. Hence this chemical inertness possessed by the noble metals accounts for their extensive use in dentistry for the making of metallic appliances, which have to be worn more or less permanently in the mouth.

The following table is a list of the chief metals used in dentistry, together with their melting-points, densities, and specific heats:—

	Metal.	Melting-point.	Density.	Specific Heat.
Noble Metals.	Gold (Au) . .	1063° C.	19.3	0.0316
	Platinum (Pt) . .	1755° C.	21.4	0.03203
	Iridium (Ir) . .	2360° C.	22.4	0.032
	Palladium (Pd) . .	1549° C.	12.1	0.056
	Silver (Ag) . .	960.5° C.	10.49	0.0559
	Copper (Cu) . .	1083° C.	8.945	0.093
	Aluminium (Al) . .	659° C.	2.70	0.222
	Nickel (Ni) . .	1452° C.	8.8	0.108
	Tin (Sn) . .	232° C.	$\left\{ \begin{array}{l} 7.2 \text{ (tetragonal)} \\ 6.5 \text{ (rhombic)} \\ 5.8 \text{ (grey)} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0535 \\ \text{(tetragonal)} \end{array} \right\}$
	Lead (Pb) . .	327.7° C.	11.34	0.03
	Zinc (Zn) . .	419° C.	7.1	0.093
	Bismuth (Bi) . .	271° C.	9.9	0.031
	Antimony (Sb) . .	630° C.	6.62	0.0489
	Cadmium (Cd) . .	321.7° C.	8.6	0.055
	Iron ¹ (Fe) . .	1530° C.	7.8	0.113
	Mercury (Hg) . .	-38.85° C.	13.595 (0° C.)	0.0333

Besides a few simple metals, certain metallic substances, *e.g.* **bronze** and **brass**, were known in ancient times, and were for a long time regarded as distinct metals. Such substances are in reality mixed metals or **alloys**. The two mentioned are alloys of copper and tin, and copper and zinc respectively. The physical properties of an alloy are often almost independent of the properties of the constituent metals, and in dentistry, except in the case of pure gold for conservative purposes, pure unalloyed metals are never used since no one metal possesses the physical properties required for any particular purpose.

Metallurgy (lit. "the working of metals"), which includes the methods of extraction of the metals from the ores, their purification, and the study of their properties, is the most ancient branch of

¹ The physical properties of the various forms of iron in commercial use, *e.g.* cast iron, wrought iron, steel, etc., vary considerably.

chemistry, and occupies a very important place in the study of materials used in dentistry.

The non-metallic inorganic substances used in dentistry comprise :—

Polishing powders, *e.g.* **pumice, chalk, whitening, rouge, and putty powder.**

Grinding materials, *e.g.* **sandstone, corundum** or emery, and **carborundum.**

Setting materials, *e.g.* **plaster of Paris** and **osteo-cements.**

Refractory materials, *e.g.* **porcelain** and **fireclay.**

Fluxes, *e.g.* **borax** and the **alkali carbonates.**

Moulding materials, *e.g.* **plaster of Paris, sand, and French chalk.**

Anæsthetic, **nitrous oxide.**

The organic substances of importance, used in dental practice, may be classified as follows :—

Cleansing agents or detergents, *e.g.* **soap.**

Antiseptics, *e.g.* **phenol.**

Denture materials, *e.g.* **caoutchouc, gutta-percha, and celluloid.**

Impression substances, *e.g.* **waxes, gums, and resins.**

Anæsthetics, local and general, *e.g.* **cocaine, novocain, and ether.**

PART I

METALS AND ALLOYS

CHAPTER I

GENERAL PROPERTIES OF THE METALS

THE most obvious property of metals is that they in general exhibit a characteristic lustre when in mass, and which they lose when finely divided. Several of them are translucent when in thin plates, and while many of them are white or grey in appearance, some well-known metals possess characteristic colours, *e.g.* gold is yellow, copper is red, while bismuth has a pink tinge. The true colour of metals is difficult to judge, on account of their usually possessing such high reflective power.

The table given on page 23 shows that the physical properties of the metals vary considerably among themselves. Whereas mercury, the only liquid metal at ordinary temperatures, has a melting point of -39° C., the melting-point of iridium is in the neighbourhood of 2300° C. The specific gravity of an individual metal may vary according to the process to which the metal has been subjected. The specific gravities of the metals which come under our survey vary from 2.7 for aluminium to 22.4 for iridium.

As a class, the metals are very much better conductors of heat and electricity than the non-metals, and the order of the thermal conductivities of the common metals, beginning with the metal of highest conductivity, is :—

Silver, copper, gold, aluminium, zinc, cadmium, palladium, platinum, tin, nickel, iron (steel), lead, antimony, mercury, bismuth.

The order of their electrical conductivities is :—

Silver, copper, gold, aluminium, zinc, nickel, cadmium, palladium, platinum, iron (steel), tin, lead, antimony, mercury, bismuth.

The **malleability**, *i.e.* the property of being permanently extended either by rolling or hammering, and **ductility**, *i.e.* the property of being drawn out into wire, are properties which depend on the high degree of plasticity combined with great strength which the metals generally possess. Thus, the metals, unlike soft substances, only suffer permanent deformation when subject to forces of considerable magnitude. The

malleability and ductility of the metals vary with the temperature and the important application of the metals in dental practice largely depends on these properties.

The malleability of the metals is determined by measuring the reduction in thickness effected by hammering or rolling when cold and without annealing, and the order of malleability is different according to the manner in which the reduction in thickness takes place. By rolling, the order from the most to least malleable of the metals commonly employed is :—

Gold, silver, aluminium, copper, tin, lead, platinum, zinc, iron, nickel.

By hammering, the order is :—

Lead, tin, gold, zinc, silver, aluminium, copper, iron, platinum, nickel.

The ductility of a metal also may vary with the temperature, and hence the temperature at which different metals are made into wire by forcing through a die varies considerably. The order of ductility is :—

Gold, silver, platinum, iron, nickel, copper, aluminium, zinc.

Another important feature of the metals is their crystalline nature. If the surface of a metal be examined microscopically after suitable polishing and etching, and before being worked by swaging or hammering, the crystalline nature of the metal will be seen. After the swaging has been continued for some time, the metal will generally have become hard and unworkable. If now the surface be examined microscopically as before, it will not exhibit the previous crystalline structure. This crystalline structure will be superficially replaced by a film of amorphous or glassy material, which possesses certain striation markings, as viewed under the microscope. These are known as “slipbands,” and are due to the layers of atoms in the crystals sliding over one another during the working. When the worked metal is annealed, the glassy metal crystallises again, and then the working can be continued. The temperature of annealing varies with the metal. It is worth remarking that tin and lead anneal even at the ordinary temperature, and therefore these two metals cannot be retained permanently in the glassy or amorphous condition.

It is the exception rather than the rule for the simple metals to be used in the arts, and this is especially the case in dentistry. The properties of a particular metal require to be modified to make it more ideal for fulfilling a particular purpose, and therefore advantage is taken of the characteristic property possessed by metals, viz., that of forming alloys. Since the physical properties of alloys are, in general, by no means those which could be calculated from their

components and the corresponding properties of the components, it is clear that the metals in an alloy are not merely in juxtaposition, forming a more or less uniform mixture. All alloys are crystalline: the crystals are of the same kind when the alloy is truly homogeneous, or the crystals may be mixtures of different kinds, some of them pure metals, some compounds, and some solid solutions.

Molten metals often mix with one another in all proportions, but numerous cases of partial miscibility have been described, the fact that zinc and lead, when melted together, separate into layers, is made use of in Parke's process for the desilverisation of lead.

Certain non-metallic elements, *e.g.* oxygen, sulphur, phosphorus, carbon, and silicon, and compounds, *e.g.* cuprous oxide (Cu_2O), cuprous sulphide (Cu_2S), ferrous sulphide (FeS), and iron carbide (Fe_3C), will also dissolve in molten metals forming crystalline solid solutions. Such substances have a profound influence on the properties of the metals, and play an important part in many metallurgical processes. They may be valuable constituents, as shown in the varieties of steel, or deleterious impurities in a metal or alloy.

If two metals be fused together, so that the resultant liquid is homogeneous, and then allowed to crystallise, the constituents of such a binary alloy may behave almost exactly like a saturated solution of common salt in water, when submitted to cooling, where the two constituents under suitable conditions separate more or less completely, giving rise, in the case of the metals, to an **eutectic alloy**. The metals which behave in this manner are not generally closely related to each other, *e.g.* lead and tin, and lead and silver form eutectic alloys. When the two metals are very similar or closely related, they may remain in **solid solution** after crystallisation of the alloy. Such alloys are perfectly homogeneous, and each consists of only one kind of crystal, which contains both metals. Thus, antimony and bismuth, which are chemically similar and isomorphous, mix in all proportions in the liquid and solid states. Silver and gold, gold and platinum, iron and nickel, and nickel and cobalt are pairs of metals which also give solid solutions. When there are marked differences between the two metals, the binary alloy may contain definite **compounds** of the two metals. The chemical formulæ of such intermetallic compounds rarely bear any relationship to the ordinary chemical rules of valency, as shown by the following examples:—

Compounds of gold and aluminium, Au_4Al , Au_2Al , AuAl_2 .

Compound of silver and tin, Ag_3Sn .

Compound of magnesium and zinc, MgZn_2 .

Compounds of mercury with sodium and potassium, NaHg_4 , NaHg_2 , NaHg , KHg_2 , KHg .

These examples also show that two metals may form more than one compound.

The mechanical properties of an alloy will, it is clear, depend on its structure. The properties of an eutectic alloy, in which the metals separate completely from each other on crystallisation, should not be widely different from what would be expected from a composite structure of this kind. When the metals form a solid solution, it is generally found that the alloy is harder and more elastic than either of the constituents. Possibly, when the crystals contain different kinds of atoms, as in a solid solution, the different layers of atoms tend to slip over one another less readily than when the atoms composing a crystal are all of one kind, as in a pure metal. When the constituents of a binary alloy form one or more chemical compounds, the difference in properties between the alloy and the individual metals is still more marked. Intermetallic compounds are frequently characterised by great brittleness; sometimes this brittleness is combined with great hardness, and then the compound is a very valuable constituent of the alloy.

Since the mechanical properties of an alloy depend not only on the nature of the constituent metals, but also on the structural composition of the alloy, the investigation of the structure of alloys is of fundamental importance to all who deal with the application of metals or alloys in the arts. In the present work, only the briefest outline of the nature of such investigations can be given, and for the proper study of metallography, reference should be made to standard works on the subject.¹ Considering for the present the case of a binary alloy, consisting of two metals, A and B, which are completely miscible in the molten condition, it has already been pointed out that on crystallisation the two metals may form an eutectic alloy, a chemical compound, or a solid solution. It should be remembered that the determination of the structure is further complicated by the fact that the solid alloy, while being uniform in character, need not necessarily be homogeneous, *e.g.* the binary alloy may consist of an eutectic of A and B, with excess of either A or B; it may consist of a chemical compound of A and B, together with an excess of either A or B; it may consist of a compound mixed with a solid solution; it may consist of two solid solutions, and so on. Further, simple metals and compounds may undergo allotropic or polymorphic changes during solidification, and compounds themselves may even undergo decomposition during the same process. Thus, the structure of a binary alloy may be excessively complicated, and the actual research work involved in its elucidation very considerable.

The metallographic study of metals and alloys is carried out chiefly

¹ *Metallography*, by Professor C. H. Desch, D.Sc., Ph.D., published by Longmans, Green & Co.

Metallic Alloys, by G. H. Gulliver, D.Sc., published by Griffin & Co., Ltd.

Chimie des Métaux et Métallurgie Dentaires, par Boll et Bennejeant, 1922, published by J.-B. Baillière et Fils.

by microscopical and physical methods, and of the latter the most important is the **thermal or pyrometric study** of these bodies on heating and cooling. The principle of the method may be illustrated by considering the behaviour of water on being cooled. If a mass of water be cooled from a temperature below its boiling-point to a temperature below its freezing-point, then, if steps are taken to prevent super-cooling, it will be found that the lowering of the temperature of the water goes on steadily until the freezing-point is reached, *i.e.* until ice begins to appear, and then the temperature remains steady until the whole mass has frozen, after which the cooling proceeds regularly as

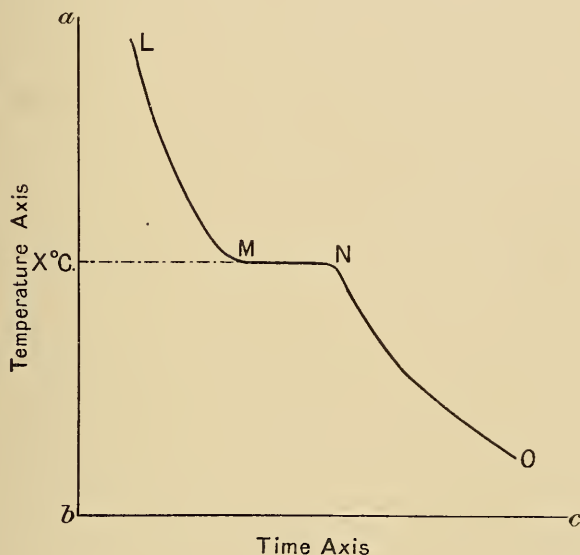


FIG. 1.

before. Similarly with a pure metal cooling from the liquid to the solid condition. If the observations be plotted in a suitable manner they will appear somewhat as shown in Fig. 1. Obviously such a diagram indicates by the "arrest" at *MN* that a change of state has taken place at a temperature of $X^{\circ}\text{C.}$, and that, on account of the latent heat of fusion of the metal, the temperature of the solidifying metal remains steady in spite of the external cooling, until the whole of the metal is frozen. The cooling curve shown in Fig. 1 is general for all pure substances whether elementary or compound, on passing from the liquid to the solid condition without any other change. The curve *LM* represents the rate of cooling of the liquid, and *NO* represents the rate of cooling of the solid.

The cooling curve of a liquid, which consists of a small amount of

substance B dissolved in A, and does not form a solid solution with it, will be of a somewhat different type from that shown in Fig. 1. When solidification of such a liquid begins, substance A will commence to separate, and the resulting liquid being richer in B, will have a lower freezing-point. Consequently the first arrest will not be parallel to the time axis (*bc*) of the diagram, but inclined to it, as shown at *MN* in Fig. 2. When a certain amount of substance A has separated, it is found that the temperature now remains constant during the complete solidification of the whole. This is represented by the arrest *NO*, parallel to the axis *bc*. At the temperature $X^{\circ}\text{C}$ (Fig. 2), the eutectic

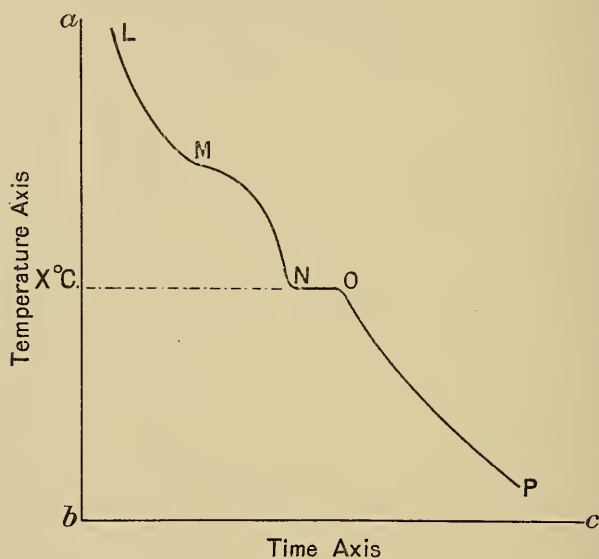


FIG. 2.

mixture of A and B separates. The composition of the eutectic mixture of any pair of substances is perfectly definite, and the eutectic point is also rigidly defined, just like the freezing-point of a pure substance. In Fig. 2 the curve *LM* represents the rate of cooling of the solution, and *OP* the rate of cooling of the solidified eutectic mixture.

When the two substances A and B do not form a compound or an eutectic but a solid solution, the cooling curve is of a still different type, represented in Fig. 3. The arrests are still defined, but the curve suffers less obvious change in direction. During solidification, A and B are continuously separating, forming crystals containing both metals, and the cooling curve consequently shows no portion parallel to the time axis.

Since changes in the nature of substances, whether due to the

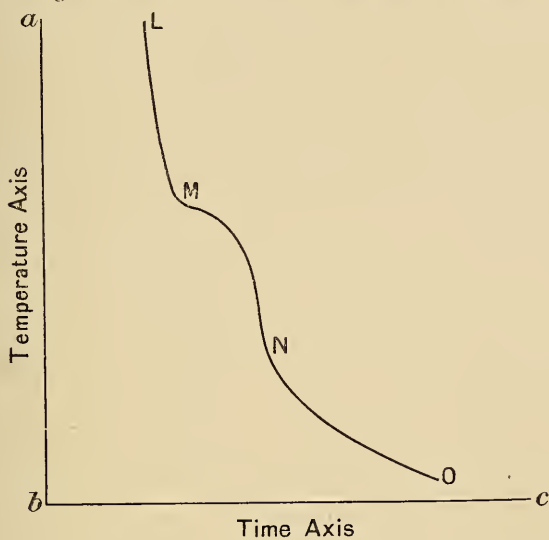


FIG. 3.

passage from the liquid to the solid condition or vice versa, or due to

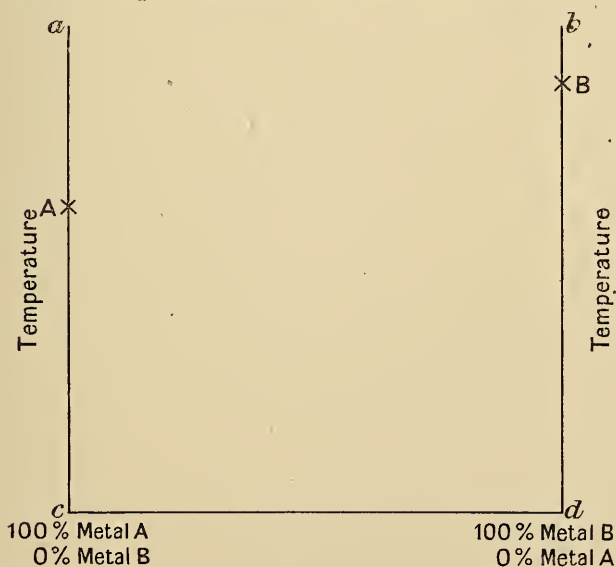


FIG. 4.

the formation or decomposition of a chemical compound, or again due

to allotropic or polymorphic change, are, in general, accompanied by heat changes, valuable information can obviously be obtained as to the constitution of alloys by plotting their cooling curves. In carrying out such investigations on a binary alloy, a large number of cooling curves of different mixtures of the constituents are plotted, and the "arrests" finally plotted on such a diagram represented in Fig. 4. The ordinates, ac and bd , are the temperature axes, while the abscissa, cd , represents the composition of the different alloys of the metals A and B, varying from a composition of 100 per cent. of A to 100 per

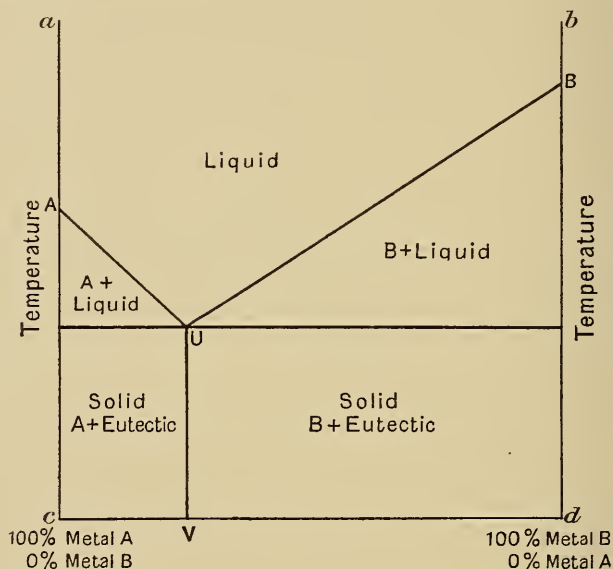


FIG. 5.

cent. of B. The points on the temperature axes will represent the freezing-points of the pure metals A and B respectively.

Bearing in mind that the freezing-point of a substance, A, is lowered by admixture with substance B, the type of diagram obtained in the case of two metals which form an eutectic alloy is represented in Fig. 5. The freezing-points of the pure metals having been determined in the manner indicated, they are marked at points A and B on the diagram. The line AU represents the freezing-points of an infinite number of mixtures of metal A, with gradually increasing quantities of B. Similarly the line BU represents the freezing-points of mixtures of B with increasing quantities of A. If we start with a liquid alloy, consisting of a small quantity of metal B dissolved in excess of A, and cool it until crystallisation just commences, the metal which separates will be pure metal A. On removing the solid metal, the liquid remain-

ing will be richer in B, and its freezing-point will be lower. By determining the freezing-points of such a series of alloys of A and B, containing increasing proportions of B, and plotting them on the diagram, the line AU is obtained. Conversely, starting with a liquid alloy, consisting of a small quantity of metal A dissolved in excess of B, on cooling, the crystals which separate will be pure B, while the

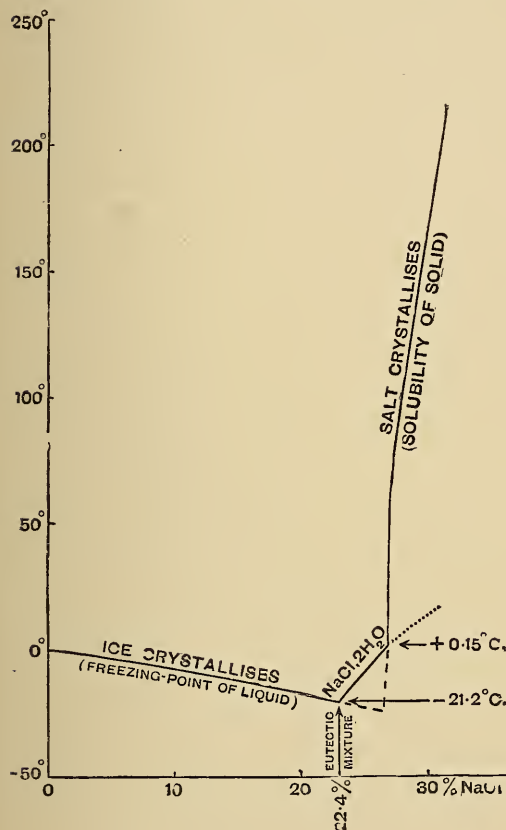


FIG. 6.—EQUILIBRIUM-DIAGRAM FOR SALT AND WATER.

temperature will be the same as that of the solid mixture separating. Such a mixture is called the **eutectic alloy**, and the temperature of solidification the **eutectic point**. In Fig. 2 the solidification of the eutectic is represented by the line NO . The eutectic alloy has, like the cryohydrate of common salt and water (Fig. 6), a rigidly defined composition, given by the position of point V on the horizontal axis, and it is, like the cryohydrate referred to, a mixture and not a compound.

When the two metals, A and B, in an alloy form a chemical com-

liquid remaining will be richer in A and have a lower freezing-point. This is represented by the line BU . From whichever way the process is started, a point will eventually be reached when, with a liquid alloy consisting of a certain concentration of metal A and metal B, the two metals, A and B, will separate together on solidification. During solidification of such an alloy the temperature will remain perfectly constant as long as liquid alloy is in contact with the two metals, even although external cooling is taking place, and, moreover, the composition of the liquid alloy at that tem-

pound, the freezing-point diagram is of a different type, and easily distinguished from the former. A chemical compound of two metals, just like any other chemical compound, has a definite freezing- and melting-point,¹ and the freezing-point curve of an alloy consisting of two metals, A and B, which are completely miscible in the molten condition, and which form a chemical compound, would be represented by such a diagram as Fig 7, while the cooling curve of the liquid compound alloy would be similar to that represented diagrammatically in Fig. 1. The freezing-point of a metallic compound, AB, would be lowered by the presence of excess of metal A or metal B, corresponding to the effect of metal B on the freezing-point of metal A, and vice versa.

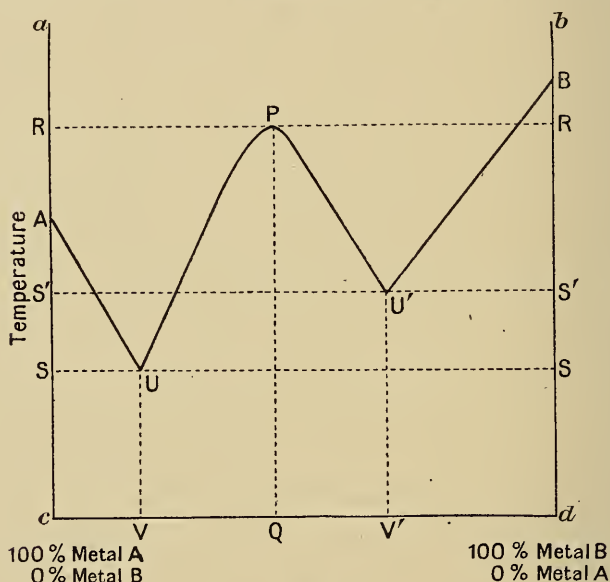


FIG 7.

In Fig. 7 two eutectics are represented at U and U' , while P represents the freezing- and melting-point of the compound. The composition of the compound is represented by the position of Q on the axis cd , X and its freezing-point is given by the position of R on the axes ac and bd . Eutectic alloy, U , consists of a mixture of the metallic compound AB, with excess of A; its composition is given by the position V on the axis cd , and its freezing- and melting-point by the position of S on the axes ac and bd . Eutectic alloy, U' , consists of a mixture of the compound AB with excess of B; its composition is defined by the

¹ Intermetallic compounds, as a rule, suffer slight decomposition in the neighbourhood of their freezing-points; but this does not call for special reference in the present work. For fuller details, such works as Desch's *Metallography* should be consulted.

position of V' on the axis cd , and its melting- and freezing-point is given by the position of S' on the axes ac and bd . As before, points A and B represent the freezing- and melting-points of the pure metals, A and B , and the lines AU and BU' are the freezing-point curves of metal A with increasing quantities of B , and of B with increasing quantities of A respectively.

In the case of a binary alloy whose constituent metals are completely miscible in the molten condition, and which form solid solutions (isomorphous mixtures) on crystallisation, the solid crystals separating from the fused alloy contain both metals, and consequently

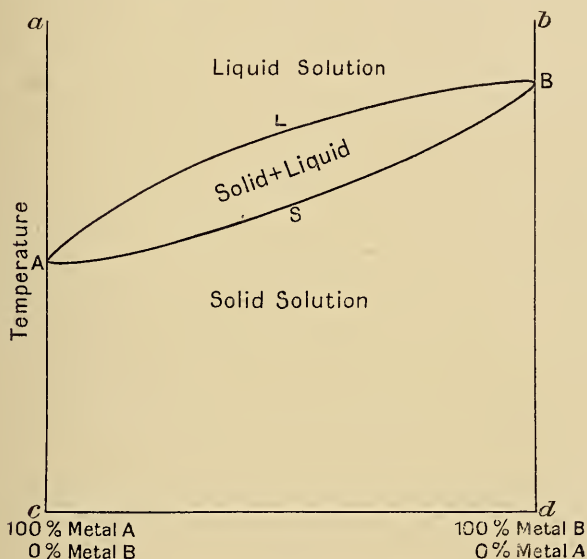


FIG. 8.

the residual liquid may be stronger or weaker in one of the constituent metals according to the composition of the solid which separates. Since the composition of the solid is different from that of the liquid from which it separates, the freezing-point and the melting-point of the alloy, unlike that of a pure metal, compound or eutectic, will not be the same. The type of freezing-point curve is represented diagrammatically in Fig. 8. In this diagram, the upper curve ALB , represents the temperatures of incipient freezing of alloys whose compositions are given by corresponding points on the horizontal axis, cd , and is known as the **liquidus**. The lower curve, ASB , represents the temperatures of incipient melting, and is known as the **solidus**.

The diagrams, Figs. 5, 7, and 8, illustrate the essential differences between pure substances, whether pure metals or compounds, eutectic

alloys, and solid solution alloys.¹ Pure substances have a definite freezing-point identical with the melting-point, and this freezing- or melting-point is lowered by the presence of another substance, and, moreover, the metal or alloy is homogeneous. Eutectic alloys have a definite freezing-point, also identical with the melting-point. Eutectic alloys are not homogeneous, they are intimate mixtures of the constituent metals, and their freezing-point or melting-point is raised by the presence of excess of either of the constituent metals. Solid solution alloys may or may not be homogeneous according as to whether the time of cooling has been sufficiently long to allow of complete equilibrium between the crystals taking place. Solid solution alloys are characterised by the fact that the freezing-point of the alloy is different from the melting-point, as illustrated in Fig. 8.

In actual practice the freezing-point curves are in general very much more complicated than the types represented above. As already indicated, the curves may be complicated by the possibility of heat changes during cooling of the liquid and solid alloy due to the formation of allotropic forms of pure metals, and polymorphic forms of compounds. Further, compounds may be formed or decomposed during the cooling of the solid alloy, and instances have already been given of two metals forming more than one compound.

The alteration in properties of an alloy according to the rate at which it is cooled from a high temperature bears on this point, and the variation in properties of the various steels illustrate it in actual practice. If there exists a transition temperature, above which one condition is stable and below which a different one is stable, then, during slow cooling, the transformation from one condition to the other may be possible. If, on the other hand, the alloy be rapidly cooled from a temperature higher than the transition temperature, the change of the form stable at the high temperature may take place so slowly that it may not actually take place, or, in other words, the condition only stable at high temperatures may, on account of the rapid cooling, persist at the ordinary temperature. Thus, if iron, which contains more than 0.85 per cent. of carbon, be rapidly cooled from a temperature higher than 700° C., an extremely hard and brittle variety of steel is obtained compared with that which is produced by slow

¹ Only the very simplest types of freezing-point curves of binary alloys are here represented diagrammatically. In the case of some pairs of metals, *e.g.* nickel and manganese, manganese and copper, which form solid solutions, the freezing-point curve passes through a minimum. The freezing-point curves of some binary alloys containing metals which form inter-metallic compounds are not of the simple W-type, but show a series of discontinuous curves, the completion of the W-portions not being possible on account of the instability of the compound or compounds. The V-shaped curve, indicating the formation of an eutectic mixture, is complicated in cases where the constituent metals do not separate in the pure condition from the still molten alloy, but as solid solutions of the two metals.

cooling. The reason for this, and for the elucidation of the properties of the almost infinite variety of modern steels, has been made clear by studying the cooling curves of the iron-carbon alloys. In the particular instance mentioned, the reason is that at a temperature above 700°C . solid solutions of carbon in iron exist, but at lower temperatures these are unstable, and if the amount of carbon is suitable, it combines with the iron, forming the compound, Fe_3C , known as **cementite**. If the carbon content be more than that required to form the compound, the remainder separates as graphite. Thus steel hardened by rapid cooling from a temperature higher than 700°C . contains the carbon in solid solution, which is metastable at the ordinary temperature, but its rate of transformation is so slow under ordinary atmospheric conditions that the metastable condition persists practically indefinitely. On the other hand, steel which has been cooled extremely slowly contains its carbon in the form of cementite. During the slow cooling the transformation from the state of solid solution to the compound has had time to take place, and a soft variety of steel is the result. Further, if hard steel (with its carbon in the state of solid solution) be heated to temperatures of $200\text{--}300^{\circ}\text{C}$., the transformation from the hard and metastable state to the soft state (with the carbon combined in the form of cementite) takes place at such a rate that it can be regulated, and hence there is the possibility of being able to reduce the hardness of steel to any required extent.

The other chief method of investigating the structure of metals and alloys is by the microscopic examination of a suitably prepared surface illuminated by reflected light. The surface is prepared for examination by cutting and grinding a small flat area, the fine polishing of this surface to remove physical irregularities, and the treatment of this surface by etching with suitable reagents, *e.g.* nitric acid, sulphuric acid, hydrochloric acid, iodine, potassium cyanide, ammonia, etc., so as to indicate the nature and structure of the metal. When viewed by reflected light, the polished surface before etching is featureless and uniformly bright. In etching, the reagent gradually dissolves the metals. The solution does not take place uniformly over the whole surface, and differentiates clearly and consistently the various constituents of metals and alloys.¹

Although there may be only one constituent, *e.g.* as in a pure metal or alloy consisting entirely of a pure intermetallic compound, the crystal structure is revealed by etching. Such a homogeneous substance consists of an aggregate of minute crystals, which have grown together so closely that the boundaries of the crystals are determined not by the natural crystal faces, but by the mutual interferences of adjacent crystals. In section, such a structure exhibits a network of roughly polygonal areas, and the etching agent attacks these areas at

¹ For actual details, the more standard works on the subject already referred to should be consulted.

different rates, producing both differences of level and varieties of surface, which readily reveals the arrangement of the constituent crystals. The same type of surface is exhibited by metals and homogeneous alloys. The homogeneous alloy may be a pure compound, or it may be a solid solution. In the latter case, the true structure may only reveal itself after more or less prolonged annealing, which is necessary to ensure the final equalisation of composition of the crystals by diffusion.

When the alloy is not homogeneous, although each constituent is built up of aggregated crystals, the difference of solubility in the etching agent between the different constituents is very much greater than that between adjacent crystals of the same constituent. Consequently

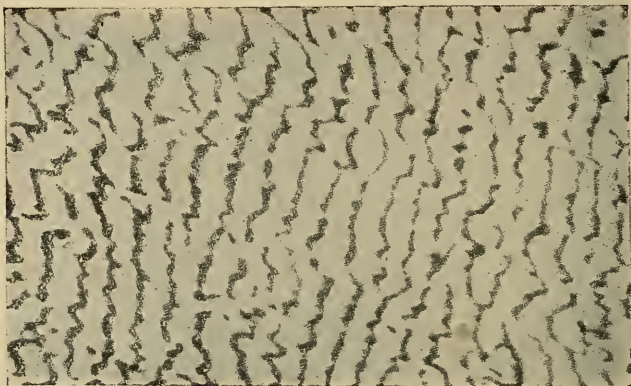


FIG. 9.—EUTECTIC ALLOY OF TIN AND LEAD.

(White=tin, black=lead. Notice the predominance of tin in the eutectic alloy ;
cf. page 107.)

in heterogeneous alloys, the etching reveals not so much the crystal structure of any of the constituents as their distribution (Fig. 9).

The above examples are sufficient to indicate that, from a microscopic study of the etched surface of an alloy, the structure of the alloy can be determined.

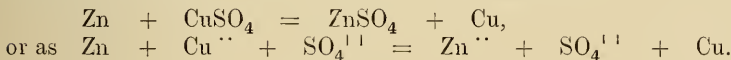
Other physical methods for investigating the structure of alloys are based on measurements of thermal expansion, electrical resistance, density, etc. ; but none of these methods have so far yielded such fruitful results as the two methods of which an introductory account has been given.

The chemical investigation of alloys beyond determining the chemical nature of the metals in the alloy does not generally give very much indication as to the structure of the alloy. In certain cases, however, a certain amount of useful information may be obtained by the careful chemical examination. Thus, some iron-carbon alloys will dissolve in dilute hydrochloric acid, leaving little or no residue,

and with evolution of hydrogen and some smaller quantity of hydrocarbons. On the other hand, other iron-carbon alloys, under the same conditions, give rise to hydrogen and little or no hydrocarbon, but leave a residue of insoluble carbon. This indicates fairly conclusively that the carbon was present in a different condition in the two classes of alloys. In the former case, it was present in a state of chemical combination as the compound Fe_3C , while in the latter case it was present as the free element, which may have been either free or in a state of solid solution in the alloys.

The use of metals in dentistry for conservative, prosthetic, or orthodontic purposes is obviously restricted by what may be termed their "chemical activity" when in contact with an electrolyte of the nature of the oral fluids. When only one metal is present in the mouth, the problem is comparatively simple, and from a knowledge of the behaviour of a particular metal when in contact with dilute acids, a solution of hydrogen sulphide and dilute alkalis, a decision can generally be made as to whether, on chemical grounds, a particular metal is suitable for a particular purpose. On the other hand, it more frequently happens that there may be more than one metal present in the mouth, *e.g.* a gold denture plate and amalgam fillings, and a knowledge of the order of the chemical activity of the metals is then of great importance.

If a piece of zinc be placed in a solution of copper sulphate, the zinc gradually goes into solution, forming zinc sulphate, and metallic copper is deposited. The action may be represented:—



In a similar manner, zinc will displace tin, lead, mercury, and a number of other metals from aqueous solutions of their salts; again, magnesium will displace zinc, while iron will not displace either magnesium or zinc, but will displace tin, lead, and mercury. It would thus appear that we can arrange the metals in a list such that a metal in the list will displace those that follow it from solutions of their salts, and be displaced from its solutions by those which precede it in the list.

Another and much more satisfactory method of determining such an order of activity of the metals is based on measurements of the electromotive force of voltaic cells when different metals are used as electrodes. The electromotive force of a cell with zinc as the cathode is found to be greater than when certain other metals, *e.g.* iron and platinum, are used instead of zinc, whereas, when certain other metals, *e.g.* aluminium and magnesium, replace the zinc, the electromotive force is increased. By carrying out careful quantitative experiments, using equivalent solutions and keeping the other conditions the same, it is found possible to arrange the metals in a series representing the difference of potential in volts, which is developed between metals

and solutions of their salts in contact with them. Such a series of the metals is called the “**potential**” or “**electro-chemical series of the metals.**”¹ In this series, in which the alkali metals, sodium, potassium, etc., occupy the highest place, the order of the metals with which we are chiefly concerned is :—

- | | |
|--------------|---------------|
| 1. Magnesium | 10. Antimony |
| 2. Aluminium | 11. Bismuth |
| 3. Manganese | 12. Copper |
| 4. Zinc | 13. Mercury |
| 5. Cadmium | 14. Silver |
| 6. Iron | 15. Palladium |
| 7. Nickel | 16. Platinum |
| 8. Tin | 17. Gold |
| 9. Lead | 18. Iridium |

This list shows not only the order in which the metals displace one another from solutions of their salts, but it also indicates the order of their chemical activity. Thus, it is at once obvious that the so-called “noble” metals occupy the lowest position. They are displaced by all the other metals, and their chemical activity is also less than that of any of the others.

The oxides of the metals from and including mercury are completely decomposed on heating leaving the metal, while the oxides of the metals from and including zinc are reduced to the metal by heating in a current of hydrogen, and these two classes of oxides differ again from the oxides of magnesium, aluminium and manganese, which are not reduced to the metal by heating in a current of hydrogen. The metals down to, and including, lead displace hydrogen from dilute solutions of mineral acids, although the hydrogen is not necessarily always obtained as such, whereas the metals from and including antimony do not generally displace hydrogen from the acids. This fact is probably related to another regarding the occurrence of the metals in nature, since, with the exception of those which have been found in meteorites, none of the metals which displace hydrogen from the mineral acids occur free in nature.

Apart from the list giving the order of displacement of the metals from solutions of their salts, it may be noted that the further apart the two metals are in the list, the greater the amount of heat liberated when the displacement occurs, *e.g.* when magnesium precipitates silver from a solution of silver nitrate, more heat is evolved than when it replaces tin under similar conditions. The replacement of one metal by another in some cases is complete, and can be used as a method of quantitative analysis.

¹ For further details, see *Principles of Inorganic Chemistry and Outlines of General Chemistry*, both by W. Ostwald.

Since the metals from magnesium to lead (inclusive) are the more easily oxidised and more readily attacked by acids, their use in the mouth is undesirable from a chemical point of view, while this objection cannot be urged against the use of the metals less easily attacked, viz., antimony to iridium (inclusive). But for the use of particular metals in the mouth other properties have to be considered, *e.g.* some metals are more toxic than others, and the above list does not indicate this except in so far as toxicity of metals may be dependent on their solubility. Further, the rate of solubility of a metal in a particular solvent, whether acid or alkaline, depends on the state of aggregation of the metal; metals in bulk are generally less readily attacked than when finely divided.

When more than one metal is present in the mouth, the above list indicates that the electromotive force of the electric current generated between two metals in contact with an electrolyte will be greater when the metals are widely apart in the list than when they are close to each other. Consequently, as far as possible, if dissimilar metals have to be employed, the metals chosen should be as near as possible to each other in the list so as to reduce to a minimum the possible generation of local electric currents in the mouth. Such electrolytic action is likely to give rise to disintegration of fillings and harmful effects to the oral tissues.

CHAPTER II

GOLD: PURPLE OF CASSIUS: COHESIVE AND NON-COHESIVE GOLD: ALLOYS OF GOLD USED IN DENTISTRY: ASSAY OF GOLD ALLOYS

GOLD—Au (Atomic Weight=197.2); Valency 3 and 1.

Occurrence.—Practically all the gold extracted is found in the native or free condition. Native gold is never chemically pure, always containing silver in varying amounts, often small quantities of iron and particularly copper, while small quantities of the platinum metals are frequently also admixed with the gold. What is known as **rock gold** occurs in small particles distributed in hard rocks, chiefly composed of quartz. Where these rocks have been subjected to high temperatures the gold may be found in veins as in South Africa, and in some cases the rocks have been so acted upon by air and water (weathering) as to be reduced to a state of subdivision, and as in California, Australia, and N.W. Canada, the *débris* has been washed down into river beds. In these districts **alluvial gold** is found at or near the surface of the beds of what have been rivers at some bygone time, and it is extracted by washing away mechanically the lighter *débris* from the heavier gold particles. Owing to the characteristic property of gold of being welded at the ordinary temperature, the alluvial gold, subjected to continuous hammering by pebbles in the river, has frequently been converted into rounded grains or nuggets (**nugget gold**) of various sizes. A famous Australian nugget weighed as much as 1.5 cwts., and was equivalent to a cube of gold of rather more than 6 inches side.

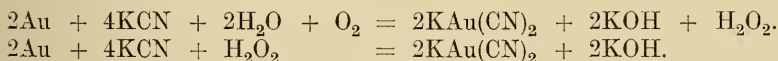
Extraction of Gold.—The supply of gold largely depends on the economical working of poor ores, using somewhat costly machinery and chemical operations, which have been so thoroughly investigated that it now pays to work ores containing less than four parts of gold per one million parts of ore.

Mechanical and Amalgamation Processes.—When necessary, the mined ore is crushed and the broken pieces separated by hand so as to eliminate obviously worthless pieces. The crushed ore is then ground either dry between steel rollers or in water by mechanical pestles. The resulting mud is mechanically splashed through fine sieves to keep back insufficiently crushed pieces, and thrown against amalgamated copper plates, by which the greater part of the gold is retained as gold amalgam. The escaping auriferous mud, or tailings, is run on an endless band, which inclines upwards to a gentle stream of water which washes away the light and worthless mud, leaving a richer gold

mud known as concentrates. The concentrates is then either treated again by the amalgamation process or by one or other of the chemical processes.

Gold readily amalgamates with mercury, which rapidly penetrates every part, and the gold can only be recovered from the amalgam by driving off the mercury by heating. Gold amalgam is soluble in excess of mercury, and when the mercury is in considerable excess, the amalgam is quite fluid. As the quantity of gold increases, the amalgam becomes viscous, and the excess of amalgam is then probably in suspension, and it can be separated from the solution by squeezing in chamois leather bags. The pasty amalgam thus separated by filtration is then heated, at first slowly, and finally to a dull red heat, when the mercury distils off, and the gold is left. The mercury so recovered, by distillation, and the filtrate, which, of course, contains a small amount of gold, is then available for further use, the small amount of gold left in it apparently accelerates further amalgamation of gold. If the pasty gold amalgam be treated with dilute nitric acid, excess of mercury is dissolved by the acid, and a highly crystalline product remains of composition approximating to AuHg_3 .

Chemical Processes.—The concentrates and finely crushed low grade ores are usually worked up by the **cyanide** (McArthur-Forrest) **process**. After preliminary roasting to remove sulphur and other volatile impurities, the material to be extracted is digested with a 0·4 per cent. aqueous solution of potassium cyanide. Now-a-days, sodium cyanide has replaced the much more expensive potassium cyanide, but the reaction is exactly analogous to that which takes place when the latter substance is employed. In the presence of the oxygen of the air, the gold goes into solution as potassium or sodium aurocyanide, and the solution is easily separated from the remaining mud. The action is described as going in two stages :—



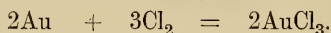
The mud left is agitated again with a more dilute cyanide solution, so as to make certain that no, or merely a negligible quantity of, gold remains undissolved. There are two processes for obtaining the gold from the cyanide solution. One is by precipitation by means of zinc, when the action taking place is :—



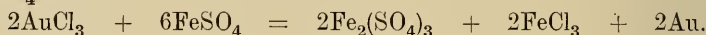
and the other process is by electrolysis, using a lead cathode on which the gold is deposited. In the former case, the gold slime is dried and roasted to volatilise any contaminating zinc, then melted and cast into ingots ready for final purification. In the latter case, the cathode is cupelled to get rid of the lead in a manner to be described later.

What is known as the **chlorination process** is also used for the

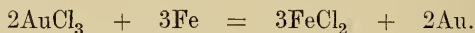
working up of concentrates and low grade ores. The ore, reduced to a fine state of subdivision, having been mixed with water, chlorine, preferably under pressure, is passed into the mixture contained in suitable vessels. The chlorine combines directly with the gold, forming the compound auric chloride, AuCl_3 , which is readily soluble in water,



From the solution which is drawn off, the gold is precipitated as a brown powder by a suitable reducing agent, *e.g.* ferrous sulphate, FeSO_4 :—



The brown powder of gold is washed with dilute acid to remove any iron, etc., dried and cast into ingots ready for refining. Many metals, *e.g.* zinc and copper, can also be used as precipitants for gold, but, as we have already seen, these metals will also precipitate silver, and this is a disadvantage attaching to their use. The reaction using iron as a precipitant is :—

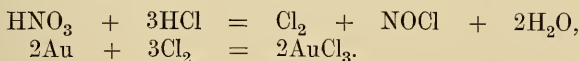


Refining of Gold.—If the crude gold obtained by any of the above processes has been found by “assay” (see p. 52) to be nearly pure, it is only necessary to melt it under suitable conditions under a suitable flux, *e.g.* sodium carbonate (Na_2CO_3), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and sodium nitrate (NaNO_3); the last named substance is added to oxidise any small quantity of base metal which may be present. If lead be present, ammonium chloride (NH_4Cl) is also added to convert it into lead chloride (PbCl_2), which, being volatile at a red heat, is easily got rid of. Generally speaking, the base metals are converted into oxides, which when fused readily react with the carbonate or fused borax, forming easily fusible slags, which are easily separated from the gold, which melts at a much higher temperature. This method of purifying gold is particularly useful in gold recovery from waste material in the laboratory, *i.e.* on the small scale. When large quantities of gold, and especially gold containing silver in amounts varying from 4 to 15 per cent. according to the source of origin of the gold, have to be refined, such a method is not suitable.

In Miller's **chlorination process** for the refining of gold, the crude gold containing silver and base metals is melted in a suitably prepared fireclay crucible, and, while molten, chlorine is passed in through a fireclay tube passing through the cover, and reaching to the bottom of the crucible. The base metals and the silver are converted into chlorides, while gold chloride, being unstable at such a temperature, is not formed. The chlorides of the base metals being volatile escape in dense fumes through an aperture in the lid, while the silver chloride, which fuses at a lower temperature than gold, is easily separated from

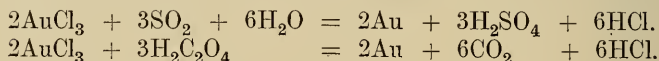
the metal by pouring off when the latter has solidified. The operation is at an end when brown fumes and chlorine escape.

The process of **parting** or **quartation** depends on the fact that silver can be completely dissolved by nitric or sulphuric acid from a gold-silver alloy, containing not more than 25-30 per cent. of gold. The crude gold, which must not contain more than 10 per cent. of copper or 5 per cent. of lead, is first melted with silver in such a proportion that the gold-silver alloy resulting after eliminating the base metals, will contain about one quarter of its weight of gold; hence the name of the process, "quartation." The crude gold-silver alloy is first melted and granulated by pouring the molten alloy into water, and then boiled first with concentrated sulphuric acid and then with dilute sulphuric acid, since silver sulphate is somewhat sparingly soluble in the former. Under these circumstances the sulphates of silver and of the base metals go into solution, and the gold remains as a dark powder, which can be treated again if necessary. The metal is then washed thoroughly and cast into ingots. The silver can be recovered from the acid solution by precipitation. Nitric acid (sp. gr.=1.2) may be used instead of concentrated sulphuric acid, but on the large scale the latter acid is to be preferred. By these methods, and with efficient working, gold containing as little as 0.5 per cent. impurity can be obtained, but the impurity is often much greater. For removing the last traces of impurity, the metal is dissolved in **aqua regia** (three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid). Solution takes place at the ordinary temperature, but as the reaction slackens, it is necessary to heat the mixture to about 100° C. The gold goes into solution as auric chloride :—



The solution is evaporated almost to dryness on the water bath, so as to drive off excess of acid, and, after being diluted considerably with purified water, allowed to stand. Any silver originally present will have been converted into silver chloride, and this will be almost completely precipitated on standing. If platinum was originally present, this will be in solution as platinic chloride (PtCl_4). To get rid of this a solution of potassium chloride is added, together with a volume of alcohol, equal to the volume of the original solution. On standing, the platinum will be completely precipitated as potassium platinichloride (K_2PtCl_6), which can be filtered off. The filtrate can be evaporated free from alcohol on the water bath. The resulting solution of auric chloride is then treated with a suitable precipitating agent, which should not be a metal on account of possible contamination of the gold. Neither should it be a reducing agent like ferrous sulphate, since traces of iron might be precipitated with the gold by possible small quantities of base metals. The precipitating agent

should, however, be a reducing agent, and sulphurous acid (H_2SO_3) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) are suitable reducing agents at this stage. The former precipitates the gold as a dark brown powder, and the latter precipitates it in a crystalline, spongy or amorphous condition according to the concentration and the temperature of the solution.



The precipitated gold is washed carefully first with dilute acid, then with a dilute aqueous solution of ammonia, and finally with purified water. Finally it is melted under borax and a little potassium hydrogen sulphate (KHSO_4) and cast into an ingot. The purity of the gold so obtained should not be lower than 99·80 per cent., and may be as high as 99·98 or 99·99 per cent.

Properties of Pure Gold.—It is a lustrous yellow metal crystallising in the cubic system. Light reflected many times from its surface becomes orange-red in hue, and consequently, when the metal is beaten into very thin leaf, or when melted or vaporised, it transmits the complementary greenish light. When finally divided, as obtained by precipitation, it may reflect or transmit light of various colours, ranging from violet or blue through purple to brown.

The density of gold is 19·3, and it varies slightly according as to whether the metal is cast or hammered, but it is restored to the normal value by annealing. Its ductility and malleability are greater than those of silver; 2 kilometres of the finest gold wire weighs only 1 gram, and gold leaf can be obtained in thickness of 0·00014 mm. In tenacity it is inferior to copper, silver, and iron; a pure gold wire of 0·127 cm. diameter requires a weight of nearly 32 kilograms to break it, while it stretches almost one-third of its original length before breaking. Its specific heat is 0·0316, and less than that of silver, whilst its thermal conductivity is also lower than that of silver. Next to silver and copper, gold is the best conductor of heat and electricity. Gold melts at 1063° C.

Gold is unaffected by dry or moist air at all temperatures. It is also unaffected by hydrogen sulphide and acid vapours generally. It is not attacked by dilute or concentrated acids, so that it remains as a brown powder when an alloy containing it is treated with nitric or sulphuric acid. Gold,¹ however, is readily soluble in aqua regia (see p. 45) or in any acid liquid in which chlorine, bromine, or iodine is evolved, and in a mixture of concentrated sulphuric acid and manganese dioxide, which evolves oxygen.

Pure gold is used in dentistry chiefly as a filling material. Its unique property of being easily welded at ordinary temperatures, com-

¹ Gold does not dissolve in any single acid, with the exception of the uncommon acid, selenic acid, H_2SeO_4 .

bined with its softness and malleability, make it perfectly adaptable to the walls of a tooth cavity. From its chemical inertness, we know that it cannot be acted upon by the oral fluids, and it cannot form injurious salts and stain the tooth tissues. It is also used as a solder for platinum.

What is known as **spongy gold** is made by slowly heating gold amalgam to redness in a muffle furnace, whereby the mercury is volatilised. If pasty amalgam is used, the gold is left in a somewhat dense form. When the crystalline amalgam, *i.e.* the residue remaining after treating the pasty amalgam with dilute nitric acid, is used, a light form of spongy gold is left. The different forms in which crystalline gold is obtained are due to differences in the condition of precipitation depending on the nature and strength of the precipitant or precipitating solution, the strength of the gold solution and the temperature. **Shredded gold** is described as being prepared by precipitation of gold from its solution by means of a warm solution of glucose or gum arabic. Crystal gold is prepared electrolytically by passing a small current through a dilute solution of auric chloride, using an anode of pure gold and a cathode of platinum. The gold from the anode goes into solution, and gold is deposited on the cathode in crystals varying in size with the strength of the solution and the current density.

What is known as **Purple of Cassius** is obtained by adding a solution of stannous chloride very gradually to a solution of auric chloride. Under these conditions the Purple of Cassius is obtained as a purple-violet precipitate, which probably consists of a stannic hydroxide coloured by colloidal gold. Purple of Cassius is used as a constituent of the frit for producing the pink gum colour of porcelain glaze (see p. 133). For dental use, Purple of Cassius is generally prepared by the dry method, which consists in treating an alloy of silver, gold, and tin with nitric acid. The alloy is made by melting together 240 parts by weight of silver, 24 parts of gold, and 17·5 parts of tin in a clean crucible under cover of borax, and then granulating by pouring into cold water. To secure homogeneity of the alloy, it is advisable to remelt and granulate as before. The granulated alloy is then treated with pure concentrated nitric acid in an evaporating dish on a hot plate. Under these circumstances the whole of the silver is dissolved out of the alloy as silver nitrate, and the tin is oxidised, forming hydrated stannic oxide, which becomes associated with, or absorbs, the metallic gold forming Purple of Cassius, which remains at the bottom of the dish as a residue. It is collected, thoroughly washed with hot water, and dried. It is then ready for mixing with the other ingredients which constitute the "gum frit."

Cohesive and Non-cohesive Gold.—All gold which has been refined by the methods described above, and is clean and dry, possesses the properties of cohesiveness and softness. These properties are, in general,

lost by alloying with other metals, although it is possible to alloy gold with small quantities of silver, copper, or palladium without seriously impairing its cohesiveness, but the alloy is harder than the original gold. The cohesiveness of gold is entirely destroyed by the addition of a small proportion of lead or antimony. To retain its cohesiveness unimpaired, pure gold should be carefully protected from the air and dust, and it should not be manipulated with the fingers. Superficial moisture and grease render pure gold non-cohesive.¹ Cohesive or pure gold should be annealed at a temperature not higher than dull redness before use. During the heating the gold should not be exposed to a naked flame, as there is always the possibility of contamination with gaseous products and of local overheating. The annealing not only serves to drive off any volatile superficial contaminating substances, but also renders the gold softer. Overheating renders the gold hard. Although it is harsher than pure and cohesive gold, a combination of pure gold and platinum foils may be employed when greater hardness is required in the filling material. The gold-platinum foil is used in the same way as pure gold, usually in the form of foil. This foil is produced by sweating an ingot of pure gold to one of platinum or one of platinum between two of gold, the combined ingot being rolled to the required thickness. As the gold gradually alloys with the platinum, the alloy becomes much paler than pure gold, the actual shade depending on the proportion of platinum.

Up to the middle of the nineteenth century, no advantage was taken of the cohesive property of pure gold in connexion with its use as a filling material. In fact, up to this time, gold was worked for dental purposes in such a manner as to counteract this property. Gold fillings consisted of small pellets tightly wedged into the cavity, and, consequently, the use of gold as a filling material was limited to cavities with strong walls or cavities so shaped that the force exerted on the gold pellets during mastication could only tend to wedge them more firmly together. Gold in this form is still employed, and is known as **non-cohesive gold**. Since the characteristic property of pure gold is its cohesiveness, whereby it is capable of being welded at the ordinary temperature, it would therefore appear that non-cohesive gold is more or less impure gold. It has been pointed out that the alloying of gold with other metals, especially lead and antimony, diminishes or destroys its cohesiveness, and, since the cohesiveness of gold is at least temporarily destroyed by surface contamination, as a result of manipulation with the fingers, we may conclude that non-cohesive gold is the cohesive variety (*i.e.* pure gold) which has undergone some surface contamination.

Non-cohesive gold is prepared in a variety of ways, some of which

¹ The cohesiveness of greasy gold foil is said to be at least partially restored by washing with a suitable solvent, *e.g.* chloroform, which is capable of dissolving the grease.

are apparently trade secrets. One variety is prepared by exposing pure gold to the action of ammonia gas, and the cohesiveness of this is restored by annealing, when any superficially "absorbed" gas would be driven off. In another variety the superficial contamination is effected by treating the pure gold foil with a solution of an iron salt, and the cohesiveness of this gold is not restored by annealing. Still a third variety, having a corrugated, crystalline structure, is obtained by heating the cohesive (pure) gold foil between paper leaves in a suitable press contained in an iron box. During the heating the paper becomes slowly charred and shrinks, corrugating the foil; the charred paper is afterwards carefully removed, but the products of the charring of the paper effectively contaminate the surface of the gold.

Non-cohesive gold actually is neither softer nor harder than the pure and cohesive gold, the difference being merely superficial. Pieces of non-cohesive gold slide readily over each other, and the foil shows no tendency to cling as pure gold foil does. Where the particular purpose allows its use, non-cohesive gold is a very valuable material; almost perfect adaptation can be obtained more easily and more quickly than with pure gold. Occasionally the actual filling may be completed with pure gold, and sometimes non-cohesive gold is used in combination with tin, both metals being in the form of foil twisted together and cut into suitable pieces ready for insertion. The gold does not alloy or cohere with the tin, the two metals remaining quite distinct from one another.

Alloys of Gold.—It has already been pointed out that pure gold, while finding successful use as a filling or conservative material, is too soft for the construction of denture plates, whether cast or swaged, and similar prosthetic appliances. By alloying gold with certain other metals, its softness and pliability may be suitably diminished without seriously affecting its resistance to chemical action. Such gold alloy must be resistant to the action of the oral fluids, and it must be sufficiently malleable and tenacious, and its colour must not be materially different from that of pure gold. Further, its melting point must be sufficiently high, so that a suitable hard solder may be employed with it.

On the English system, gold alloys are described according to the carat or quantity of gold which they contain. **Pure gold** is described as of **24 carat**, and the various qualities of gold alloys are described as of 9, 12, 15, 18, 20 or 22 carat, according as they contain 9, 12, 15, 18, 20 or 22 parts by weight of gold respectively per 24 parts by weight of alloy. According to the continental and American system, **pure gold** is described as being **1000 fine**, and various alloys are designated as, *e.g.*, 900 or 750 fine, according as they contain 900 parts or 750 parts, etc., by weight of pure gold per 1000 parts by weight of alloy. Since 24 carat gold, *i.e.* pure gold, corresponds to 1000 fine gold, it is easy to calculate the quality of a gold alloy on either system when its

standard on the other system is known. Thus, 23 carat gold is $\frac{23 \times 1000}{24}$ fine, and 9 carat gold is $\frac{9 \times 1000}{24}$ fine, and so on. Each country has its standard gold represented by its coinage. The British standard is 22 carat, *i.e.* $\frac{22 \times 1000}{24}$ or 916.7 fine. It contains 2 parts by weight of copper per 24 parts by weight of alloy, or 83.3 parts of copper per 1000 parts by weight of alloy. In German, American, and Italian coinage, standard gold is of 21.6 carat, *i.e.* 900 fine.

Copper forms a complete series of solid solutions with gold: the freezing-point curve of the copper-gold alloys passes through a minimum at about 880° C., the gold content of the alloy, which melts at this temperature, being about 82 per cent. (Fig. 10). Since the melting-points of gold and copper are 1063° C., and 1083° C. (respectively), the marked lowering of the melting-point of gold by copper

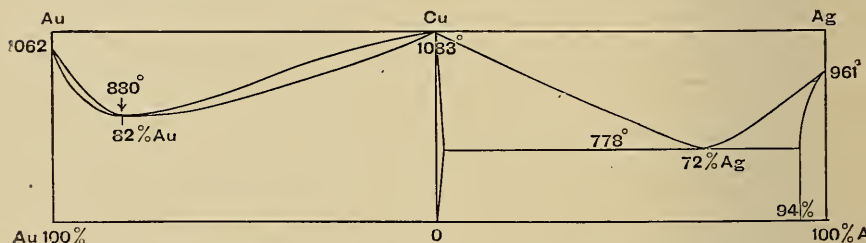


FIG. 10.—FREEZING-POINT CURVES FOR ALLOYS OF COPPER, SILVER, AND GOLD.

and of copper by gold are at once illustrated. Copper imparts a reddish colour to gold, and renders the gold distinctly tougher and harder, as shown by the following figures quoted by Roberts-Austin¹:—The purest gold has a tenacity of 7 tons to the square inch, and it elongates 30 per cent. before breaking, whereas standard gold, which contains 8.33 per cent. by weight of copper, has a tensile strength of 18 tons to the square inch, and stretches 34 per cent. before breaking.

Silver, on the other hand, has comparatively little influence on the tenacity or extensibility of gold. Silver alloys with gold in all proportions, and forms solid solutions with it; the freezing-point curve of the alloys of the two metals lies entirely between the freezing-points of the two metals, and a gold-silver alloy, containing from 0.1 to 4 per cent. of silver, has a melting-point very little different from that of pure gold (Fig. 11). Silver has a marked effect on the colour of gold, the alloy containing 50 to 60 per cent. of silver being almost white. In Fig 11 the liquidus and solidus curves of the silver-gold alloys are not separated. They lie very close together, and this indicates that the solid alloy varies but little in composition from that of the liquid alloy with which it is in contact.

¹ *Introduction to the Study of Metallurgy*, page 117.

The use of platinum for alloying with gold for the making of springs and clasps has already been referred to. Platinum alloys with gold in all proportions (Fig. 11); the two metals are isomorphous, and form solid solutions, and the freezing-point curve lies entirely between the freezing-points of the two components. Platinum diminishes the yellow colour and malleability of gold, but it increases its strength and elasticity; and, unlike the effect of copper, it raises the melting-point.

These three metals, viz., copper, silver, and platinum, have been found the most useful for alloying together with pure gold so as to make it suitable for the making of prosthetic appliances of

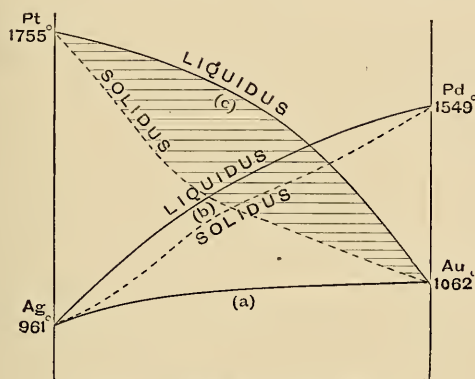


FIG. 11.—FREEZING-POINT CURVES FOR ISOMORPHOUS METALS.

(a) Gold and silver, (b) Palladium and silver, (c) Platinum and gold.

various kinds. If silver and copper are to be alloyed with gold, the latter is first melted in a suitably prepared crucible, and the silver added before the copper, *i.e.* in the inverse order of their fusibility. To minimize the oxidation of the copper, the molten gold or gold-silver alloy is covered with a layer of charcoal powder before the copper is added. If platinum is to be incorporated in the alloy, this metal is added after the copper in the form of very thin foil, which quickly dissolves in the molten alloy. In actual practice, pure gold is seldom used for alloying. The starting-point for making a desired alloy is usually standard gold (22 carat), chiefly because its properties are such that it is much less liable to contamination than pure gold, and because it bears its own certificate of purity.

The amount of these metals used for alloying with gold for prosthetic purposes depends on the particular purpose for which the alloy is to be used. The following tables give the composition of the chief gold alloys used for various purposes :—

GOLD DENTURE ALLOYS

Carat	18		19			20			22
Pure gold . . .	18	..	19	19	..	20	20	..	22
Standard or coin gold . . .	..	19.6	..	..	20.7	..	..	21.8	..
Copper . . .	4	2.4	3	1	1.3	2	2	..	1
Silver . . .	2	2	2	3	2	2	1	2.2	0.75
Platinum . . .	..	..	..	1	..	..	1	..	0.25
	24	24	24	24	24	24	24	24	24

GOLD CROWN ALLOYS

Kind of Crown.	Ordinary.				Sec-tional.	Seam-less.	Bridge.
Carat . . .	20	21.6	22		21.6	21.6	17.1
Pure gold . . .	20	..	21.6	22	21.6	21.6	17.1
Standard gold . . .	..	21.8	..	..	..	..	..
Copper . . .	2	..	1.2	1	0.8	0.6	3.5
Silver . . .	2	2.2	1.2	0.75	1.6	1.8	1.7
Platinum . . .	..	..	..	0.25	..	..	1.7
	24	24	24	24	24	24	24

GOLD ALLOYS FOR CLASPS, BANDS, SPRINGS, ETC.

Carat	20		18		16	
Pure gold . . .	20	..	18	..	16	..
Standard gold . . .	..	21.8	..	19.6	..	17.5
Copper . . .	2	..	3	1.4	5.3	3.8
Silver . . .	1	1.1	1	1	2.7	2.7
Platinum . . .	1	1.1	2	2	..	..
	24	24	24	24	24	24

Assay of Gold.—From the above it is clear that it is often of the utmost importance to know quantitatively the amount of gold in an alloy used in dental practice, and for this purpose an “**assay**,” as it is termed technically, of the gold has to be made. The method of

assay by means of a **touchstone** is at the best only very rough, the results are by no means accurate, and it is of little value with alloys of 18 carat and upwards. It is, however, of some value as a preliminary determination, as giving an approximate idea of the quality of the alloy, and this approximate result is of value in the carrying out of an accurate assay.

The touchstone is usually a piece of fine-grained dark jasper, and occasionally common slate is used instead. The stone is scratched by drawing a corner of the alloy across it, and the streak so made compared with that of similar streaks made by scratching the stone with points of gold alloys of known carat, termed "touch-needles." The streaks are further tested and compared by means of a drop of nitric acid or dilute aqua regia. The streak from the alloy of lower carat is acted upon more readily than that made by the richer alloy, and the more copper there is in the alloy, the deeper is the green colour produced by the acid. By having a number of touch-needles made from alloys of known composition, the carat of the alloy in question is determined by observing which needle gives a colour nearest in colour and reaction to that made by the alloy.

The normal and **accurate assay** of gold in an alloy is made by **cupellation** and **parting**. A sample (usually about 0.5 gram) of the alloy to be assayed is accurately weighed by means of a special assay balance, and the alloy, together with rather more than twice its weight of pure silver, cut into small pieces, is wrapped in a piece of pure assay lead foil, weighing about six times the weight of the sample of alloy. The whole is placed on the cupel, a shallow crucible made of calcium phosphate or bone ash, about 1.5 inches in diameter, previously heated, and heated at first gently and finally more strongly in a muffle furnace. Under these conditions the lead is oxidised to lead monoxide or litharge (PbO), and any copper in the original alloy to cupric oxide (CuO). These oxides are absorbed by the cupel, which may take up as much as its own weight of the oxides. When all the lead has been oxidised and the lead oxide absorbed, the residual molten metal changes markedly in appearance. It can be removed from the cupel by throwing into pure water, and the solid button brushed free from particles of bone ash. The button thus obtained now contains nothing but gold and the silver present in the sample. It is rolled and annealed into a ribbon and twisted into a spiral or "cornet," and this is heated very carefully, first with dilute, and later with strong nitric acid. The silver goes into solution as silver nitrate, and the metal can be subsequently recovered from the acid solution. The gold is left as a thin "cornet," very like brown paper in appearance, and it has to be handled with the greatest care. The gold cornet, after careful washing and drying, is heated in the muffle, when it shrinks and assumes the more normal appearance of gold, and is finally weighed accurately. From this result the carat of the original alloy can easily be calculated.

If the original alloy contained platinum, the latter would remain with the gold after the above treatment, and it would have to be separated by the method described under the "refining of gold" (p. 44). Where very great accuracy is required, check assays on gold of known standard are carried out along with the ordinary determination, so as to enable any loss of gold by vaporisation to be determined, and due allowance made.

The oxides of certain metals, especially tin and antimony, are not absorbed by calcium phosphate, and if the original alloy contains such metals cupellation has to be preceded by a process known as **scorification**. In this process, the weighed alloy is heated to red heat with about twelve times its weight of pure lead in a shallow fireclay saucer or scorifier in a muffle furnace. A portion of the lead is oxidised to lead monoxide, but this is not absorbed by the fireclay, but combines with it, forming a fusible compound or slag, which gradually covers the surface of the charge. The metals tin and antimony are oxidised at the same time, and these oxides are absorbed by the slag, and are thus removed, while the unoxidised metals, gold and silver, remain alloyed with the excess of lead. After cooling, the slag is chipped away and the resulting "button" cupelled in the manner already outlined.¹

The actual **calculation of the carat of an alloy** of known gold content is readily made, as the following examples will illustrate:—

(a) *Calculate the carat of an alloy containing 8 parts of pure gold, 2 parts of copper, and 2 parts of silver by weight.*

The total weight of the alloy = 12 parts, of which 8 parts are pure gold. Therefore 24 parts of the alloy will contain $\frac{8 \times 24}{12} = 16$ parts of pure gold. That is, the carat of the alloy is 16.

(b) *Calculate the carat of an alloy containing 80 parts of standard (i.e. 22 carat) gold, 10 parts of copper, and 20 parts of silver.*

The total weight of the alloy = 110 parts. The weight of pure gold in this = $\frac{80 \times 22}{24}$ parts. Hence 24 parts of the alloy contain $\frac{80 \times 22 \times 24}{24 \times 110} = \frac{80 \times 22}{110} = 16$ parts of pure gold. That is, the carat of the alloy is 16.

The above procedure can obviously be summarised by the following rule:—

To calculate the carat of an alloy, multiply the weight of the gold by its carat, and divide by the weight of the alloy, or

$$\text{Carat of alloy} = \frac{\text{Weight of gold} \times \text{carat of the gold}}{\text{Weight of alloy}}$$

¹ For practical and fuller details of the method of assay, the reader is referred to *The Sampling and Assaying of the Precious Metals*, by E. A. Smith, published by Griffin.

The method of calculation of the amount of gold of higher carat which must be added to an alloy of known carat so as to raise the gold content of the latter, is illustrated by the following examples :—

(a) *Calculate the amount of pure gold (i.e. 24 carat) required to raise 10 dwts. of 16 carat gold to gold of 20 carat.*

$$\text{The amount of gold in original alloy} = \frac{10 \times 16}{24} = 6\frac{2}{3} \text{ dwts.}$$

$$\text{The amount of other metals in original alloy} = \frac{10 \times 8}{24} = 3\frac{1}{3} \text{ dwts.}$$

Since 20 carat gold contains 4 parts of other metals, and 20 parts of pure gold in every 24 parts by weight of alloy, therefore the weight of pure gold in 20 carat alloy is 5 times the weight of the other metals in that alloy.

Since the weight of the other metals in the final alloy is the same as that in the original alloy, i.e. $3\frac{1}{3}$ dwts., therefore the weight of the gold in the final alloy is 5 times this, i.e. $16\frac{2}{3}$ dwts.

But the original alloy contained $6\frac{2}{3}$ dwts. of pure gold, and hence $16\frac{2}{3} - 6\frac{2}{3} = 10$ dwts. of pure gold must be added to 10 dwts. of 16 carat gold to raise it to 20 carat gold.

(b) *Calculate the amount of 22 carat (i.e. standard or coin) gold which must be added to 10 dwts. of 16 carat gold to raise it to gold of 18 carat.*

$$\text{Weight of pure gold in original alloy} = \frac{10 \times 16}{24} \text{ dwts.}$$

Suppose the amount of 22 carat gold to be added = n dwts., then the weight of pure gold in this 22 carat gold = $\frac{22n}{24}$ dwts.

The total weight of the final alloy = $(10 + n)$ dwts., of which $\frac{(10 + n) 18}{24}$ dwts. is pure gold.

Since the pure gold in original alloy + pure gold in the added alloy = pure gold in the final alloy,

$$\text{hence} \quad \frac{10 \times 16}{24} + \frac{22n}{24} = \frac{(10 + n) 18}{24}, \text{ hence } n = 5 \text{ dwts.}$$

That is 5 dwts. of 22 carat gold have to be added to 10 dwts. of 16 carat gold to raise it to gold of 18 carat.

The above algebraical method is not the most straightforward method of making the calculation, but it has been used so as to deduce a brief summary of the method in the form of a rule, in the following way :—

From the above equation

$$(10 \times 16) + 22n = (10 + n)18 = (10 \times 18) + 18n$$

$$\text{hence} \quad (22 - 18)n = (10 \times 18) - (10 \times 16)$$

$$\text{therefore} \quad n = \frac{(10 \times 18) - (10 \times 16)}{(22 - 18)}$$

$$\text{and} \quad n = \frac{10(18 - 16)}{(22 - 18)} = 5.$$

That is, to obtain the weight of rich gold alloy which has to be added to a certain weight of lower carat alloy to raise the gold content to a required higher carat, multiply the weight of the original alloy by the difference between the carat required and the original carat, and divide the product by the difference between the carat of the rich gold added and the carat required, or

Weight of rich gold to be added =

$$\frac{\text{Weight of original alloy (carat required - carat of original alloy)}}{(\text{Carat of added rich gold - carat required})}$$

To lower the carat of a gold alloy, other metals (copper, silver, and platinum, either separately or together) have to be added, and the method of calculation of the amount of these "other metals" to be added, is shown in the following examples:—

(a) Calculate the amount of "other metals" which has to be added to reduce 6 dwts. of pure gold (i.e. 24 carat) to gold of 18 carat.

The weight of pure gold in the final alloy is the same as that started with, viz. 6 dwts.

Eighteen carat gold contains $\frac{18}{24}$ ths of its weight of pure gold, and $\frac{6}{24}$ ths of its weight of other metals, i.e. the weight of other metals in 18 carat gold is one-third the weight of the gold. Hence the weight of other metals to be added to 6 dwts. of pure gold is **2 dwts.** to reduce it to 18 carat gold.

(b) Calculate the weight of "other metals" which has to be added to 6 dwts. of standard (i.e. 22 carat) gold to reduce it to gold of 18 carat.

Working this out algebraically so as to deduce a summarised form or rule embodying the method, suppose the weight of other metals to be added = n dwts. As in the previous example, the weight of pure gold in the original alloy must be the same as that in the final alloy, i.e. $\frac{6 \times 22}{24}$ dwts. The final alloy weighs $6 + n$ dwts,

and, since it is 18 carat, the pure gold in it must weigh $\frac{(6+n)18}{24}$ dwts.

$$\text{Therefore} \quad \frac{(6+n)18}{24} = \frac{6 \times 22}{24},$$

$$\text{hence} \quad (6+n)18 = 6 \times 22,$$

$$\text{and} \quad (6 \times 18) + 18n = 6 \times 22,$$

$$\text{and} \quad 18n = (6 \times 22) - (6 \times 18) \\ = 6(22 - 18),$$

$$\text{therefore} \quad n = \frac{6(22 - 18)}{18} = 1\frac{1}{3}.$$

Thus $1\frac{1}{3}$ dwts. of "other metals" would have to be added to 6 dwts. of standard or 22 carat gold to reduce it to gold of 18 carat.

From the above, the method of calculation may be summarised as follows :—

To determine the weight of "other metals" which has to be added to a known weight of rich gold alloy in order to reduce it to gold of known and lower carat, multiply the weight of the original alloy by the difference between its carat and the carat required, and divide the product by the carat required, or—

Weight of "other metals" to be added =

$$\frac{\text{Weight of original alloy (carat of original alloy - carat required)}}{\text{Carat required}}$$

CHAPTER III

PLATINUM METALS AND ALLOYS: DENTAL ALLOYS: SOLDERS

PALLADIUM—Pd. (Atomic Weight=106·7). IRIDIUM—Ir. (Atomic Weight=193·1).

PLATINUM—Pt. (Atomic Weight=195·2).

AMONG the eighty-three elements known at the present time there are nine which are placed in three groups of three each, and which are known as transition elements. These are :—

- (1) Iron, At. Wt. = 55·84; Cobalt, At. Wt. = 58·97; Nickel, At. Wt. = 58·68.
- (2) Ruthenium, At. Wt. = 101·7; Rhodium, At. Wt. = 102·9; Palladium, At. Wt. = 106·7.
- (3) Osmium, At. Wt. = 190·9; Iridium, At. Wt. = 193·1; Platinum, At. Wt. = 195·2.

It will be noticed that the atomic weights of the metals in each of these transition groups are in no case very widely dissimilar, and in one or two cases they lie very close to each other. The chemical properties of the metals in each group are very similar, but the properties of the metals of the iron group generally do not bear very close resemblance to the general chemical properties of the metals of the palladium and platinum groups. The metals of the palladium and platinum groups form six precious metals, and they resemble each other so closely that their separation from one another is not readily effected.

The six elements, ruthenium, rhodium, palladium, osmium, iridium, and platinum are associated together in the metallic condition in gravels and sands chiefly in the Ural Mountains, and in smaller quantities in California, Brazil, and Australia. The platiniferous sands and gravels are washed, as in the case of the extraction of alluvial gold, leaving the “platinum concentrates,” which generally contain, in addition to the above metals, small quantities of gold, copper and iron. Since palladium, iridium and platinum are the only ones of these precious metals which are of importance for dental purposes, the others need not be described here.

The separation of the platinum metals in a pure state from each other is effected by a series of difficult and laborious operations, and for fuller details of the processes involved, specialised works on the subject should be consulted.¹ The extraction of the metals depends

¹ *The Precious Metals, comprising Gold, Silver, and Platinum*, by Sir T. K. Rose, published by Constable.

on the treatment of the concentrates with aqua regia (concentrated hydrochloric acid 3 parts, and concentrated nitric acid 1 part by volume), when the insoluble residue contains only sand and small quantities of the extremely resistant alloys, platiniridium and osmiridium. During the aqua regia treatment, osmium forms a volatile tetroxide (OsO_4), and is easily removed from the solution by distillation. The remaining solution contains the platinum and iridium as the soluble chlorides, PtCl_4 and IrCl_4 respectively—or, more correctly, as the soluble acids, hydrochloroplatinic acid, H_2PtCl_6 , and hydrochloroiridic acid, H_2IrCl_6 . When the solution is evaporated, the iridium compound is converted into iridium trichloride (IrCl_3), which is a light insoluble green powder, and when ammonium chloride is added to the solution, the platinum is precipitated as the highly crystalline yellow ammonium platini chloride, $(\text{NH}_4)_2\text{PtCl}_6$. This salt, on being heated, decomposes completely, leaving a residue of metallic platinum.

One of the numerous methods of separating palladium from the other metals associated with it consists in the precipitation of palladious cyanide, $\text{Pd}(\text{CN})_2$, by the addition of a solution of mercuric cyanide, $\text{Hg}(\text{CN})_2$, to a neutral solution of a palladium salt. The cyanide is decomposed on being heated, leaving a residue of palladium.

Iridium is usually obtained from the alloys, platiniridium and osmiridium, which are left undissolved when the “platinum concentrates” are digested with aqua regia. These alloys, which also contain small quantities of the other associated metals, are extremely resistant and hard. They can only be obtained in powdered form by alloying with a large excess of zinc, and dissolving the zinc from the powdered alloy. One process for extracting the iridium from the powdered osmiridium consists in mixing the latter with sodium chloride and heating the mixture to redness in a current of chlorine. The metals are converted into their chlorides, OsCl_4 and IrCl_3 , respectively, and osmium tetrachloride being volatile is expelled. The residue of mixed chlorides is dissolved in water in the presence of chlorine and hydrochloric acid and potassium chloride added to the solution. Under these conditions the double chlorides of iridium, platinum, etc. (K_2IrCl_6 , K_2PtCl_6 , etc.) are precipitated. This precipitate is collected, dissolved in water, and fractionally reduced with hydrogen. Iridium is the last of the metals to be reduced by this means.

Pure Palladium (from *Pallas*, one of the minor planets discovered at about the same time, 1804), is a lustrous silver-white metal, which is much lighter than gold or platinum, its density being 12.1. Its melting point is 1549.2°C ., the lowest of all the platinum metals. It is softer than platinum, it takes a high polish, and can be hammered out into fairly thin foil, and drawn into fine wire. When heated in the oxy-hydrogen flame, palladium is converted into a greenish vapour

which partially oxidises on cooling ; at a somewhat lower temperature molten palladium absorbs oxygen, which, as in the case of silver, is expelled on solidification of the metal. Its specific heat is 0.056, much higher than that of gold or platinum, and therefore, in this respect, it is a more suitable material for denture plates than either of these two metals.

Palladium is unaffected by dry or moist air at ordinary temperatures even in the presence of hydrogen sulphide ; it is tarnished rapidly by acid vapours and by the halogens. Palladium foil is readily distinguished from platinum foil by the production of a black stain when an alcoholic solution of iodine is brought into contact with it ; the stain disappears only on heating. Palladium is oxidised superficially when heated in air, and the bluish film of oxide is decomposed at a higher temperature, leaving the metal untarnished. Palladium differs from gold and platinum in being readily soluble in nitric acid, even when the latter is cold and dilute. If a large quantity of platinum be alloyed with palladium, the alloy is not attacked by nitric acid. The most remarkable property possessed by palladium is its power of absorbing or occluding hydrogen. The amount of hydrogen absorbed depends, to some extent, on the form of the palladium, and specimens have been obtained which have absorbed 900 times their volume of hydrogen. During the absorption of the gas, the metal retains its appearance, but expands in volume. It is not improbable that the product consists of a solid solution of palladium hydride, having the composition Pd_3H_{21} in palladium. Probably on account of its property of absorbing hydrogen, palladium is capable of effecting the decomposition of hydrocarbons at temperatures much lower than those ordinarily necessary, and when palladium is heated in a Bunsen flame, it swells up and carbon is liberated from the hydrocarbons. Palladium hydride is also a very powerful reducing agent, and is frequently employed for this purpose in organic chemistry.

Pure **Iridium** (from *iris*, the rainbow, on account of the varied colours of its oxides) is a lustrous steel-white metal, which has a density of 22.4, and a melting-point of 2360°C . It is remarkably hard, harder than many steels, and although brittle at ordinary temperatures, it becomes fairly malleable on being heated. Its specific heat is 0.032, and its coefficient of linear expansion is 0.00000658, *i.e.* less than that of platinum. It is stated that the metal may be worked by fusing it with phosphorus, a malleable compound being formed, from which the phosphorus may be subsequently eliminated by heating it to redness in the presence of lime.

Iridium which has been fused is insoluble in all acids, and even in aqua regia, unless alloyed with a large proportion of platinum. It is untarnishable at ordinary temperatures, and although oxidised superficially at a red heat, the oxide is decomposed at a higher

temperature, leaving the metal untarnished; in this respect iridium behaves similarly to palladium. Iridium is attacked by chlorine at a red heat, forming the trichloride IrCl_3 , and the **iridium black** precipitated from the solution of this salt by means of zinc is soluble in aqua regia. Spongy iridium, obtained by igniting the black form or ammonium iridichloride, $(\text{NH}_4)_2\text{IrCl}_6$, is also soluble to a certain extent in aqua regia.

Pure **Platinum** is a lustrous, bluish-white metal, which, like gold, crystallises in the cubic system. Its density is 21.4, and it melts at 1755°C. , a temperature necessitating the use of the oxy-hydrogen flame or the electric furnace. Platinum is nearly as soft as gold, and much softer than silver; it is highly malleable and ductile, and can be beaten into thin foil and drawn into fine wire. In these respects it ranks next to gold and silver. In tenacity it ranks next to iron, copper, and nickel; a wire, 1.3 mm. in diameter requires a load of nearly 50 kilograms to break it, or 50 per cent. more than gold. Its specific heat at ordinary temperatures is 0.03203, about the same as that of gold. Platinum has a lower thermal conductivity than gold, and, therefore, from a dental point of view, its use as a material for dentures is to be preferred over that of gold. The coefficient of linear expansion at temperatures between 0° and 1600°C. has an average value of 0.00000975, and this is the nearest of all the available metals to the coefficient of linear expansion of most forms of glass and porcelain. When melted in comparatively large masses, platinum absorbs oxygen in a similar manner to silver, and the absorbed oxygen is liberated just before the solidification of the metal, giving rise to "spitting." This does not cause any difficulty in the working of platinum, since it can be readily welded at a temperature far below its melting-point.

The lustre of platinum, like that of gold, remains unchanged in dry or moist air at all temperatures, even in the presence of hydrogen sulphide and ordinary acid vapours. Platinum has a strong tendency to combine with carbon, and, on this account, platinum vessels should not be heated by a flame in which incandescent particles of carbon are present. The metal is not attacked by the ordinary acids whether dilute or concentrated, except when alloyed with a large excess of silver (40 parts by weight of silver to 1 of platinum), when it is completely dissolved with the silver by dilute nitric acid, but not by sulphuric acid. Unlike gold, platinum is almost insoluble in cold dilute aqua regia, but it dissolves fairly readily in the hot concentrated mixture forming hydrochloroplatinic acid, H_2PtCl_6 . Like gold, it is also soluble in other mixtures which generate chlorine, and in all such cases platinum chloride, PtCl_4 , is formed. Platinum has the power of absorbing or occluding hydrogen, but not to anything like the same extent as palladium.

Platinum sponge, or spongy platinum, is obtained by igniting

ammonium platinichloride, $(\text{NH}_4)_2\text{PtCl}_6$. It is a grey porous substance, which has the power of igniting a jet of hydrogen and other combustible gases directed upon it.

One way of obtaining, what is known as platinum black, is by reducing a solution of platinic chloride by means of zinc. It is a black powder which stains the fingers like lamp-black. This form of platinum has been found to occlude as much as 800 times its volume of oxygen, and it has found considerable use as an oxidising agent. Both of these forms of platinum are converted into the compact metal by welding at a red heat.

The Platinum Metals in Dental Practice : Dental Alloys : Solders.—

From the above it will be readily appreciated that the physical and chemical properties of platinum are such as render it invaluable to the dentist. It is used as a filling material in combination with cohesive gold, more especially when the filling is required to resist great attrition. On account of the fact that its coefficient of expansion is very close to that of porcelain, it is the only metal which can be used satisfactorily in conjunction with that substance, and hence its use for the pins and backings of porcelain teeth, for lining the tubes in tube-teeth, for posts in crowns and dowels in crown and bridge work, for matrices in making fused inlays, and as a denture base in continuous gum work.

As in many other cases, the pure metal is not sufficiently hard to allow of its use in actual practice, and, for this reason, platinum is advantageously alloyed with iridium. Basins and crucibles used for special operations in the chemical laboratory are made of platinum-iridium alloys, and these alloys are used in connection with fused porcelain crowns and bridges. Platinum-iridium alloys are also used in making thermo-couples for thermo-electric thermometers or pyrometers, so largely employed in the accurate determination of temperatures necessary in the study of alloys. The addition of a small amount of iridium not only imparts great hardness to the platinum, but it also greatly increases its strength and raises its melting-point. The platinum-iridium alloy is therefore less easy to work than pure platinum, and must be swaged with zinc counter-dies. Plates of platinum-iridium alloy are, like those of pure platinum, soldered with pure gold, and the alloy used for denture plates should have an iridium content not greater than 10 per cent., but for pins and posts it may be increased to 30 per cent.

The physical and chemical properties of platinum render it highly suitable for the construction of many dental appliances, *e.g.* cauteries, spatulas, nozzles of blowpipes, small syringes, small trays for carrying the investment in porcelain work, and for the muffles of small gas furnaces and annealers. For the wiring of electrically heated apparatus, recently discovered alloys containing nickel are now being used instead of platinum. Platinum plate becomes hard and springy during

hammering, and it has the disadvantage that it can be annealed only at a full white heat, and out of contact with air. The annealing of platinum is best effected under a covering of lime in a muffle furnace, and usually requires from 10 to 15 minutes.

Platinum is usually soldered with pure gold, and, since neither of these metals is directly oxidisable, a flux is not necessary. An 18 carat gold solder does not make a satisfactory joint with platinum directly, but if a small quantity of pure gold be first sweated on to the platinum, an 18 carat or higher carat gold solder can then be employed, using borax as a flux. Gold and platinum alloy with each other and form a complete series of solid solutions, and the melting-point of all the alloys of platinum and gold lie between the melting-points of the two pure metals (Fig. 11). Alloys of gold and platinum, containing from 10 to 30 per cent. of the latter metal, are used as solders when these are required to possess a higher melting-point than the melting-point of high-fusing porcelain. On account of their high melting-point, these solders require the oxygen-coal gas or nitrous oxide-coal gas blowpipe.

What is known as "**dental alloy**" is composed of platinum and silver. These two metals probably form an intermetallic compound, having the formula Ag_2Pt , which contains about 52.5 per cent. of silver, and which forms solid solutions with silver. The actual composition of dental alloy may vary considerably, and it is used as a base for artificial dentures. With increasing proportions of platinum the malleability and ductility of the silver is diminished and the melting point raised, and its resistance to chemical reagents increased. Dental alloy of good quality contains from 20 to 33 per cent. of platinum, and is essentially a solid solution of the compound Ag_2Pt in the excess of silver. Such an alloy is malleable, ductile, and tenacious, and its melting point (about 1560°C . for a platinum content of 33 per cent.) is sufficiently high to admit of the use of a high carat gold solder. It is, however, harsher than gold in working, and is apt to tarnish under certain oral conditions. Dental alloy is also useful as a backing for porcelain teeth, and in making crown posts. Since it is not readily attacked by mercury it may be employed in the construction of retention posts in large amalgam fillings.

Dental alloy is made by melting the silver first in a plumbago crucible, and the requisite amount of platinum, in the form of fine scrap or thin foil, is added gradually. The alloy should be allowed to cool very slowly, so as to avoid liquation, and to produce a homogeneous product. If the amount of platinum in the alloy is small, hot concentrated nitric acid attacks it, dissolving all the silver and a portion of the platinum; on the other hand, hot concentrated sulphuric acid dissolves all the silver, leaving the platinum unaffected.

Palladium and silver alloy with each other in all proportions, and

form a complete series of solid solutions, the melting-points of which all lie between the melting-points of pure palladium and pure silver (Fig. 11). An alloy containing 75 per cent. of silver and 25 per cent. of palladium has been used in the place of dental alloy. Its properties are very similar to those of the silver-platinum alloy, but it is not so hard, and distinctly less elastic. Van Eckart's alloy is of a somewhat similar character, and differs from dental alloy in the partial substitution of copper for silver. It is hard, malleable, and highly elastic, but it has the disadvantage of tarnishing rapidly in the mouth. The following table shows the composition of some of these denture alloys and platinum solders :—

DENTAL ALLOYS AND SOLDERS CONTAINING PLATINUM METALS

	Dental Alloy.		Palladium Alloy.	Van Eckart's Alloy.		High Fusing Solders.	
Platinum . . .	20	33	..	12·5	25	10	25
Gold	..	..	..	..	..	90	75
Silver	80	67	75	16·8	31·3	..	..
Copper	..	..	..	68·7	43·7	..	..
Palladium . . .	..	..	25	..	..	..	..
	100	100	100	100	100	100	100

The Assay of Platinum Alloys is carried out in the following manner :

The weighed portion of dental alloy is first rolled into thin foil and is placed in a suitable covered beaker and warmed with moderately concentrated nitric acid. The whole of the silver and a portion of the platinum are dissolved, while the remainder of the platinum is left as a black residue. The solution is diluted and a rod of zinc is placed in it. The whole of the silver and the platinum formerly in solution are precipitated as a dark powder. The precipitated metals are collected and again treated with warm nitric acid when the silver alone dissolves ; the platinum being no longer alloyed with the silver is quite unaffected. The platinum is then collected and weighed. As a further check, the platinum may be dissolved in warm aqua-regia, and the solution having been freed from excess of acid by evaporation on the water-bath is treated with a concentrated aqueous solution of ammonium chloride and a volume of ethyl alcohol equal to about one half of the volume of the original solution. Under these conditions the platinum is completely precipitated as the yellow crystalline ammonium platinichloride, $(\text{NH}_4)_2\text{PtCl}_6$, which is filtered off, washed with a mixture of equal volumes of alcohol and water, and finally

decomposed by heating to redness in a weighed porcelain crucible. The weight of the platinum left should be equal to that originally dissolved.

When platinum is present in gold alloy, the button of gold remaining after cupellation (see p. 54) contains the platinum originally present. To obtain the platinum, the button is first alloyed with three to four times its weight of pure silver and the resulting alloy rolled into thin foil. On warming the foil in nitric acid, the gold is left undissolved and all the silver and platinum go into solution. The silver is first precipitated from the filtered solution as silver chloride, AgCl , and after filtering off this, the platinum is precipitated in the usual manner as ammonium platinichloride, $(\text{NH}_4)_2\text{PtCl}_6$. The platinum is obtained from this in the way described above.

Impurities in Platinum.—The ease with which platinum alloys with most of the metals greatly inferior to it in tenacity and malleability, makes it highly important to avoid heating platinum in contact with easily reducible oxides of the base metals. Platinum forms highly brittle compounds with phosphorus, arsenic, and tellurium. It has been found that when the platinum pins of porcelain teeth have snapped, the fractured ends of such brittle teeth present a crystalline appearance very different from the fibrous structure of tough platinum wire, although the metal from which the pins were made must have been highly tenacious. While such brittle pins may not contain any base metals or arsenic or tellurium, it is possible that they may contain traces of phosphorus (added to lower the melting-point of native platiniridium) or carbon (from the terminals used in the electric furnace in which the platinum may have been fused). If the brittleness is due to such causes, it could be removed by getting rid of the impurities by prolonged fusion of the metal in the oxyhydrogen blow-pipe.

CHAPTER IV

SILVER: ALLOYS OF SILVER: SILVER SOLDERS ELECTROPLATING

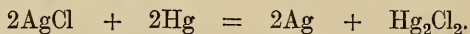
SILVER—Ag. (Atomic Weight=107.9); Valency, 1

Occurrence.—Silver occurs frequently in the metallic state, and occasionally, as in Norway and South America, it has been found in considerable quantity. Native silver usually contains gold and copper and sometimes other metals.

The most common sources of silver are ores containing its sulphide (Ag_2S), **argentite**, and its chloride (AgCl), **horn-silver**. Numerous double sulphides of silver and other metals, *e.g.* copper, arsenic, and antimony occur naturally, while most of the silver extracted commercially occurs as sulphide in lead sulphide (PbS) or **galena**. Naturally occurring gold also generally contains silver which is separated from it during the refining of the former metal.

Extraction of Silver.—One process for the extraction of silver consists in smelting the ore with metallic lead. The sulphide is thereby reduced to the metallic state and forms an alloy with the excess of metallic lead. The method of separation of the silver from the silver-lead alloy is the same as that used for the treatment of argentiferous lead by the Pattinson or Parkes process described later (p. 71). This method is known as "**cupellation**," which is carried out in various ways, only one of which need be described here. The alloy is placed on the hearth, or cupel, of a reverberatory furnace into which an oxidising atmosphere can be introduced. The hearth consists of an iron frame filled with finely powdered bone ash [calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$] which has been condensed previously by mixing with water containing a small quantity of potassium carbonate (K_2CO_3) and beating. The temperature is gradually raised to a red heat and the cupel almost filled with the alloy. Oxidation proceeds rapidly, and the lead is gradually converted into litharge (PbO). The bed of the cupel is so arranged that the melted lead oxide flows away and can be collected. Finally, the last traces of lead disappear leaving metallic silver behind.

The amalgamation processes depend on the fact that silver chloride is readily decomposed by mercury with the formation of mercurous chloride (calomel, Hg_2Cl_2) and metallic silver:—



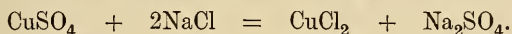
The silver so liberated then amalgamates with the excess of mercury present. These processes are therefore applicable not only to ores

containing metallic silver and silver chloride, but also to ores containing silver sulphide which is easily converted into the chloride.

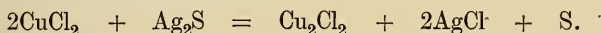
In the simplest of the amalgamation processes, the finely stamped ore is ground with mercury in large copper-lined mortars, the decomposition of the silver chloride being facilitated by the addition of copper sulphate and sodium chloride. The preliminary conversion of silver sulphide into the chloride may be accomplished in various ways. In the old Mexican process, an intimate mixture of the well stamped ore is ground up successively—by the treading of mules—with a solution of sodium chloride and crude copper sulphate, which contains iron sulphate (obtained by roasting copper pyrites) and mercury. The time of the various operations may vary from about two to six weeks.

The resulting amalgam is well washed mechanically so as to free it from lighter particles of mud and then filtered through canvas bags to remove excess of mercury. The amalgam remaining is distilled in suitable iron retorts when the silver is left behind. It can then be cast into ingots ready for refining. The chemical reactions involved are probably :—

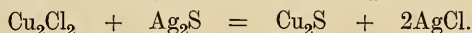
(a) A double decomposition between the copper and iron sulphates and sodium chloride whereby chlorides of copper and iron are formed :



(b) A decomposition of silver sulphide by the chlorides resulting in the formation of silver chloride :

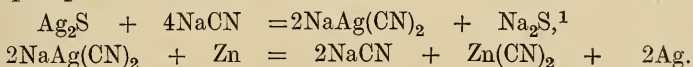


(c) The cuprous chloride thus formed dissolves in the solution of sodium chloride and acts upon other silver sulphide :



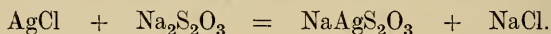
The solution of silver chloride in the solution of sodium chloride is then decomposed by the metallic mercury in accordance with the equation given above, resulting in the formation of mercurous chloride and metallic silver.

Potassium (or sodium) cyanide has been applied successfully to the extraction of silver from silver minerals in Mexico and other countries. The process is carried out similarly to that used in the extraction of gold, the cyanide solution, however, being about twice as strong (0·7 per cent. instead of about 0·3 per cent.) as for the extraction of the latter metal. The resulting sodium (or potassium) argento-cyanide, $\text{NaAg}(\text{CN})_2$, solution after filtration is treated with zinc to precipitate the silver :—

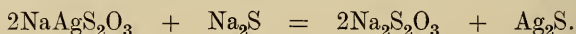


¹ Free access of air converts the sodium sulphide into sodium thiosulphate and sulphur, and so prevents the above reaction being reversed.

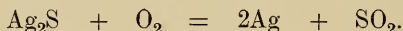
Of the so-called wet processes for the extraction of silver, only two will be described briefly here. In the **Ziervogel** process, used for the extraction of silver from argentiferous copper mattes obtained in the smelting of argentiferous pyrites, the ores are carefully roasted under such conditions that the silver and part of the copper sulphides are converted into silver and copper sulphates. The soluble sulphates are extracted with water and the silver precipitated from the solution by means of scrap copper. Other processes consist in roasting the ore with sodium chloride, by which the silver is converted into silver chloride. In the **Percy-Patera** process, the silver chloride so formed is dissolved out by means of a cold solution of sodium thiosulphate, the soluble silver-sodium thiosulphate being produced :—



The silver is precipitated from the solution by means of sodium sulphide as silver sulphide and sodium thiosulphate is regenerated :—



The precipitated silver sulphide is collected, dried and roasted and then charged into molten lead which can then be cupelled as above. Or, the sulphide is roasted in an oxidising atmosphere when crude metallic silver remains and the sulphur is got rid of as sulphur dioxide :—



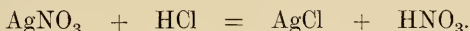
In the **Augustin** process, the silver chloride is extracted with a hot saturated solution of sodium chloride and the silver precipitated from the solution by means of metallic copper.

Silver is refined electrolytically for commercial purposes. The electrolyte is a solution of silver nitrate acidified with nitric acid. The anode or positive pole consists of impure silver and the cathode a thin plate of pure silver. Gold if present in the impure silver is precipitated as a "mud" below the anode. The concentration of the electrolyte and the current density are carefully regulated so as to avoid the deposition of copper, which may be present in the impure silver, with the pure silver on the cathode.

The preparation of chemically pure silver has been rendered necessary for the determination of the equivalent of the metal. The most recent method (Richards) started with silver nitrate which was repeatedly recrystallised from its solution in pure water. The salt was then converted into silver chloride by treatment of its solution in pure water with pure hydrochloric acid and the well washed silver chloride reduced to silver by warming with a solution of pure sodium hydroxide and invert sugar. The precipitate of silver was thoroughly washed with pure water, dried and fused on pure lime. The silver so obtained was then further purified electrolytically using a solution of pure silver nitrate as the electrolyte. The crystals of silver deposited on the cathode were finally fused on lime in an atmosphere of hydrogen

so as to remove any occluded oxygen. The silver was freed from any adhering lime by scrubbing with pure sand, washing with pure dilute nitric acid, then with a pure solution of ammonia, and finally with pure water. It was then dried by heating in a vacuum at 400°C .

More generally, silver separated in the refining of gold, or in working up laboratory residues is precipitated from its solution in nitric acid as silver chloride by the addition of hydrochloric acid or sodium chloride,



The silver chloride is collected and washed thoroughly on a filter. After drying it is fused with about twice its weight of anhydrous sodium carbonate in a plumbago crucible. Under these conditions metallic

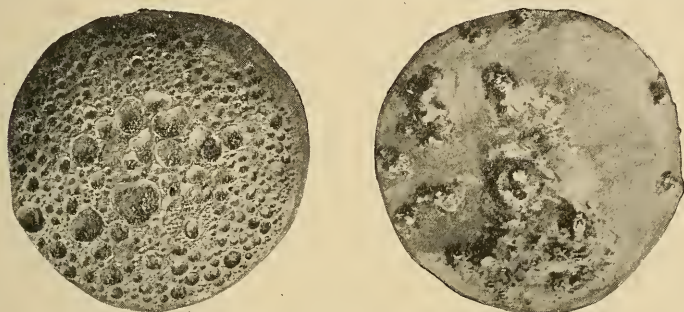
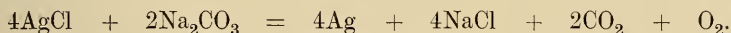


FIG. 12.—BUTTON OF SILVER SHOWING THE EFFECTS OF “SPITTING.”

silver is produced owing to the instability of silver carbonate and oxide,



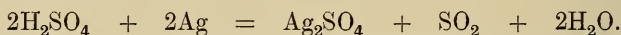
Properties of Silver.—Pure silver is a lustrous white metal having a highly crystalline fracture. Light reflected many times from its surface shows an orange-yellow tinge and the thinnest silver leaf transmits the complimentary purple-blue light. The density of silver is 10.49 and it expands considerably on fusion, the specific gravity of the molten metal at its melting-point being 9.5. In malleability and ductility, silver comes next to gold and these two metals are more malleable than all the other metals. In working, silver soon becomes hard and brittle and requires more frequent annealing than gold. The tenacity of silver is somewhat greater than that of gold; a silver wire of 0.127 cm. diameter requires a weight of approximately 39 kilograms to break it, while it stretches one-third of its original length before breaking.

The melting point of silver is 960.5°C ., and it boils at 1955°C . Stas actually distilled silver, in order to purify it, from a retort made

of pure lime heated by means of an oxyhydrogen flame. The molten metal absorbs more than twenty times its volume of oxygen which it gives up on solidification; this is the cause of the **spitting**¹ of the silver globule noticed in assaying silver unless the silver is cooled very cautiously (Fig. 12.).

Silver has a specific heat of 0.0559 and its thermal conductivity is the highest of all the metals. Similarly its electrical conductivity is the greatest of all the metals, having a relative value of 105, that of copper being regarded as the standard with a value of 100.

Silver is not acted upon at any temperature by air or oxygen, whether moist or dry. It is rapidly and superficially attacked by hydrogen sulphide and acid vapours. In the former case, the surface of the metal becomes covered with a film of brown silver sulphide, Ag_2S . Silver is readily soluble in dilute or concentrated nitric acid, and silver nitrate (AgNO_3), easily soluble in water, is formed. It is also fairly rapidly dissolved by hot concentrated sulphuric acid with the formation of silver sulphate and evolution of sulphur dioxide:—



The solubility of silver in nitric and sulphuric acids is made use of in the parting of silver and gold. Hydrochloric acid has very little action on silver, probably on account of the very small solubility of silver chloride, which salt is always precipitated when hydrochloric acid or any soluble chloride is added to a solution of a soluble silver salt.

Uses of Silver.—It has been pointed out already that silver is used as a constituent of gold alloys for denture bases and in hard solders; and, indeed, except in electroplating, pure silver is rarely used in dental practice or in the arts generally. Silver is employed alloyed with platinum and palladium for denture bases (page 63), and alloyed with tin (page 72) it forms the basis of the majority of modern dental amalgams.

Alloys of Silver.—From an industrial point of view, the alloys of silver with copper are of the greatest importance. The alloys are prepared in the same manner as the gold-copper alloys. The addition of a small quantity of copper to silver lowers its melting point, prevents “spitting” on solidification, and makes it harder without sensibly impairing its malleability or altering its colour. Silver and copper form an eutectic mixture which contains 71.9 per cent. of silver, and this eutectic, known as Levor’s alloy, has a melting point of 778° C. (Fig. 10, page 50). Silver and copper are, however, mutually soluble in each other, the limits of solubility at the eutectic

¹ The absorption of oxygen and consequent “spitting” of pure silver can be prevented by covering the metal with charcoal or sodium chloride before melting. This prevents access of air or oxygen. This procedure is unnecessary with alloyed silver, which does not absorb oxygen appreciably.

temperature are about 6 per cent. copper in silver and 1 per cent. silver in copper in the carefully annealed alloys.

The chief alloys of the silver-copper series are those used for coinage. The British Standard Silver contained 92·5 per cent. of silver, 7·2 per cent. of copper, 0·2 per cent. of lead, and 0·1 per cent. of gold; but an alloy containing 90 per cent. of silver is usual in European countries. The appearance of the etched surface of a silver coin is very different from that of a cast alloy of the same composition on account of the mechanical treatment to which the coin has been subjected. When, however, the coin has been annealed, its polished

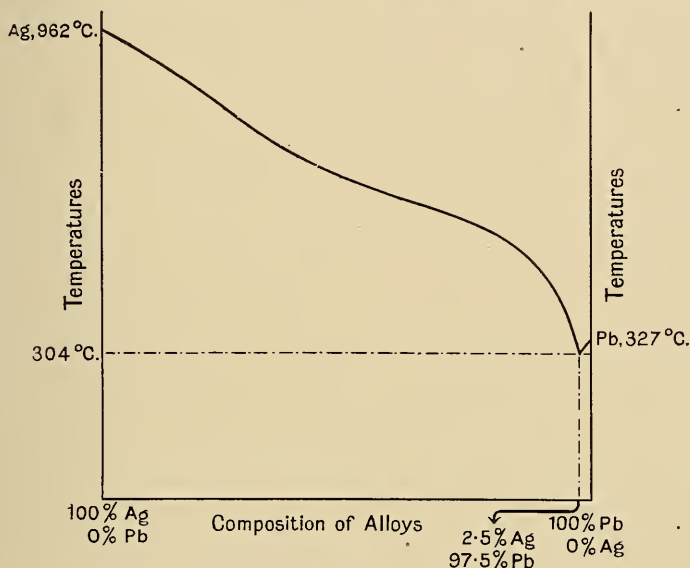


FIG. 13—FREEZING-POINT DIAGRAM OF SILVER-LEAD ALLOYS.
(Adapted from *Landolt-Börnstein*.)

and etched surface presents a similar appearance to that of the cast alloy of the same composition. Such alloys are harder and more elastic than pure silver, but, owing to the more ready oxidisability of the copper, they tarnish readily in air, especially on being heated.

When molten, silver and lead mix together in all proportions, but on solidification they separate almost completely. The two metals form an eutectic alloy, which contains 2·5 per cent. of silver, and which melts and solidifies at 304° C. (Fig. 13).

In the **Pattinson** process for the desilverisation of argentiferous lead containing not less than 2 ounces of silver to the ton, the lead alloy is melted at a temperature just a little lower than the melting-point of pure lead (327° C.), and on cooling the first crystals which separate are those of pure lead. These are separated mechanically

from the still molten alloy, which is now richer in silver. On further cooling, more crystals of lead separate, and the process is repeated until finally the eutectic temperature is reached, beyond which the separation cannot be carried further. The eutectic alloy, containing 2.5 per cent. of silver, can then be cupelled in the manner already described and the silver obtained. The lead oxide (PbO) produced in the cupellation can be reduced to metallic lead.

Silver readily forms alloys with zinc, and the latter metal is used in **Parke's** process for the desilverisation of lead. When lead and zinc are melted together in a crucible two layers are formed; the upper layer is chiefly zinc and contains about 1 per cent. of lead, while the lower layer is chiefly lead containing a little more than 1 per cent. of zinc. Any silver present in the original lead will distribute itself in accordance with the relative solubilities of silver in lead and in zinc respectively. Since the solubility of silver in zinc is greater than that in lead, most of the silver will be found in the zinc layer. If a suitable quantity of zinc be added to a silver-lead alloy containing a very small amount of the former metal and the whole melted, the alloy of zinc and silver rises to the surface during the cooling, and when it solidifies it can be withdrawn by means of a perforated ladle. It is probable that the compound, AgZn_{12} , is formed, which melts at 430°C ., *i.e.* above the melting-point of zinc (419°C .). This forms a crust in which some lead is entangled. After separation, the silver-zinc alloy is heated to a temperature slightly higher than the melting-point of lead to liquefy as much of the lead as possible, and the residue is heated in a suitable retort, whereby the zinc is distilled off and recovered. The residue in the retort is a silver-lead alloy rich in silver, and the silver can be obtained from this by cupellation.

Silver-Tin Alloys.—From a dental point of view, probably the most important alloys of silver are those containing tin, which form the basis of the majority of dental amalgams largely employed in modern conservative practice. When alloyed together, silver and tin form an eutectic which melts at 220°C . The two metals also form one compound having the formula Ag_3Sn , and all alloys containing less silver than that indicated by the formula, *i.e.* less than 73.3 per cent., are heterogeneous, and contain only the free compound and free tin. The alloys used for dental amalgams contain from 40 to 70 per cent. of silver.

The alloys of silver and tin have been carefully investigated by Joyner and Knight,¹ and these authors have critically reviewed previous work on the subject. The compound, Ag_3Sn , is capable of existing in two modifications, of which the " α " modification is the form stable below 232°C ., and the " β " form is stable above 232°C . In a series of experiments, G. V. Black² investigated the pheno-

¹ *Trans. Chem. Soc.*, 1911, 99, 195; 1913, 103, 2247; 1914, 105, 639.

² *Dental Cosmos*, 1895–1897, 35–39.

menon of the so-called "ageing" of silver-tin alloys, and he showed that, when the freshly prepared filings are amalgamated with mercury and the excess of mercury removed, the amount of mercury retained by a given weight of the freshly prepared alloy is about twice as great as that retained when the same weight of filings of the same alloy have been "aged," either by heating to 100°C ., or by standing for a considerable time at the ordinary temperature. Joyner and Knight have shown very clearly that :—

(1) "Ageing" is a property of the compound, Ag_3Sn , contained in the alloys, and a state of fine sub-division is essential for its occurrence. For alloys containing the compound, Ag_3Sn , and free tin (*i.e.* with a silver content of less than 73.3 per cent.), the phenomenon of "ageing" is roughly proportional to the amount of the compound; Ag_3Sn , present and vanishes entirely for pure tin. In the case of silver-tin alloys containing a greater amount of silver than 73.3 per cent., and which consist, if well annealed, of solid solutions of silver in the compound, Ag_3Sn , the difference between the mercury retained by aged and unaged filings is less pronounced than in the former case.

(2) "Ageing" is not due to superficial oxidation of the filings.

(3) "Ageing" is not due to contamination of the filings with adventitious impurities present as a result of their preparation.

(4) "Ageing" is complete in 20 minutes at 100°C .

(5) "Ageing" does not affect the nature of the amalgam finally obtained, provided that excess of mercury is present.

(6) No more mercury is taken up either by aged or unaged filings after a few days. The final proportion of mercury retained is the same in both cases. The sole effect of "ageing" is to retard the initial stages of amalgamation.

(7) "Ageing" of filings of silver-tin alloy, whether in coal gas or in air, is not accompanied by a change in weight. The "ageing" of the filings is, however, accompanied by an increase in density and a corresponding diminution in volume. Finally, it is suggested by the above-mentioned authors that, although the mechanism of "ageing" is as yet unknown, all the evidence so far accumulated points to its being due probably to a polymorphic change in the compound, Ag_3Sn .

Silver-Platinum and Silver-Palladium Alloys.—The alloys of silver with platinum and with palladium, which are used for denture bases, have already been described (see p. 63). Although in gold denture bases silver is present to a small extent, in the platinum and palladium alloys used for denture bases silver is the chief constituent. The silver-platinum alloy is generally known as "dental alloy."

Silver Amalgams.—Silver amalgamates with mercury, and silver

amalgams have been found in nature. Three compounds of silver and mercury have been proved to be capable of existence. These have the formulæ: Ag_3Hg_4 , Ag_3Hg_2 , and Ag_3Hg . Of these, the compound, Ag_3Hg_4 , is the most widely known as being a constituent of many amalgam fillings, and it also is the main constituent of the crystals forming the silver tree, "Arbor Dianæ," formed by allowing mercury to stand in contact with a solution of silver nitrate. It is also the only silver-mercury compound readily formed.¹

Silver Solders.—These alloys, which generally contain also copper and zinc, are frequently employed in the dental laboratory for use in uniting surfaces of brass, iron, and, especially, German silver in the construction of orthodontic appliances. Silver solders belong, like the gold solders, to the class of hard solders, as they melt at a fairly high temperature before the blowpipe. Borax is generally employed with silver solders as a flux. In making them, the silver and the copper are first melted together and the zinc added with the usual precautions against oxidation; a good hard solder may be made by adding zinc to ten times its weight of molten standard silver. The melting-point of a hard silver solder may be conveniently lowered, if necessary, by the addition of a small quantity of tin. The following indicates the composition of some silver solders:—

SILVER SOLDERS

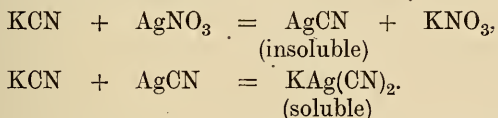
Pure Silver	..	..	80	75	..	75	74	73	62.3
Standard Silver	90.9	86	..	..	81	..	..	..	..
Copper	..	..	20	24	18	22	26	25	28.3
Zinc	9.1	14	..	1	1	2	..	2	9.4
Tin	..	..	..	..	..	1	..	..	..
	100	100	100	100	100	100	100	100	100

The assay of silver and silver alloys is effected by cupellation in the same way as that of gold, omitting, of course, the operation of quartation, and the button is weighed without parting. For standard silver, about six times its weight of pure lead foil is required, and alloys containing zinc and tin must first be subjected to scorification for the reason stated in connection with the assaying of gold.

One of the most important uses of silver is in the process of **electroplating**, whereby articles made of base metal are coated with a layer of silver. The article to be plated is made the cathode and a plate of pure silver the anode in an aqueous solution of potassium argentocyanide [$\text{KAg}(\text{CN})_2$]. The arrangement of the apparatus is similar to that employed in electrogilding. The solution, which should contain 1 to 2 per cent. of silver, is made by adding potassium

¹ Ogg, *Zeitchr. physik. Chem.*, 1898, 27. 285; Reinders, *ibid.*, 1904, 54. 609.

cyanide solution to a solution of silver nitrate until the white precipitate of silver cyanide has entirely dissolved,



For 250 c.c. of solution, 7.5 grams of each salt are required, dissolved in separate quantities of 100 c.c. of distilled water; the cyanide solution having been added to the solution of silver nitrate, the whole is made up to 250 c.c. with distilled water and thoroughly mixed.

The article to be plated, which is preferably of a white copper alloy (*e.g.* German silver), having been thoroughly cleaned and polished, is washed with hot sodium hydroxide solution, immersed in dilute nitric acid for a short time, and finally coated with a thin film of mercury by immersion for a very short time in a dilute solution of mercuric nitrate [$\text{Hg}(\text{NO}_3)_2$]. Articles made of tin, pewter, etc., are transferred to the plating solution after the preliminary cleaning. It is important to remember that tin and pewter articles should be plated in a separate plating solution, as the latter is liable to become contaminated with small quantities of base metal when tin or pewter is plated. The character of the silver deposit depends on conditions substantially identical with those in the case of electrogilding. Electroplating is, however, carried out at the ordinary temperature. It is said that the silver may be caused to deposit with a bright surface by adding a small quantity of carbon disulphide to the plating solution the day before it is used. The electroplated article, which usually presents a dull appearance, is thoroughly washed in hot water, and, after being dried with a hot duster, is burnished.

The so-called **oxydised silver** is prepared by immersing ordinary bright silver for some time in a dilute solution of sodium sulphide. The dark colour is due to the coating of the silver with a thin film of black silver sulphide (Ag_2S).

CHAPTER V

COPPER AND ITS ALLOYS

COPPER—Cu. (Atomic Weight=63·57); Valency, 2 and 1.

Occurrence.—Copper is found as the free metal in large crystalline masses in the neighbourhood of Lake Superior, but elsewhere it exists for the most part only in combination. On account of the difficulty of working the native copper, nearly the whole of the world's supply of the metal is extracted from other ores where the metal is in combination. The chief ores are :—

(a) Sulphide Ores.

Copper pyrites, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ or CuFeS_2 : a brass-coloured complex sulphide found in Spain.

Cuprous sulphide or **copper glance**, Cu_2S , which occurs in Cornwall.

Cupric sulphide or **indigo copper**, CuS , which is found in blue flexible plates in Vesuvian lava, in Chile, and in the copper mines at Mansfield.

(b) Oxide and Carbonate Ores.

Cuprous oxide, **cuprite** or red copper ore, Cu_2O is found in Cornwall.

Cupric oxide, CuO , occurs as the mineral **tenorite** at Vesuvius in black scaly crystals.

Basic cupric carbonate is found as the beautiful green mineral, **malachite**, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, in the Urals and as the mineral **chessylite** or azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, found at Chessy, near Lyons.

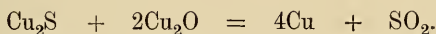
(c) Sulphate Ores.

The largest copper mine in the world is in South America and is chiefly a deposit of basic cupric sulphate, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$.

Extraction of Copper.—While copper ores may contain up to 35 per cent. of the metal, copper may be profitably extracted from material containing as little as three per cent. The material left after roasting iron pyrites in the manufacture of sulphuric acid, and known as **burnt pyrites**, is a valuable source of copper. Such materials of low copper content are treated by what is known as a wet process. This consists in roasting the ore with sodium chloride whereby the copper is converted into cupric chloride, CuCl_2 . The cupric chloride is extracted with water and the copper precipitated from the solution by means of scrap iron.

The extraction of the metal from sulphide ores containing more than 4 or 5 per cent. of copper is carried out by a dry process. This process depends primarily on two factors, the greater affinity of sulphur for copper than for iron, and the readiness of ferrous oxide (FeO) to combine with silica to form a fusible ferrous silicate. The ore is first submitted to preliminary roasting in air at a moderate temperature, when the iron sulphide is converted into oxide whilst cuprous sulphide remains unaffected. At the same time, such substances as sulphur and arsenic are oxidised to form easily volatile oxides which are thereby eliminated. The calcined ore is transferred to a hotter furnace and silica (if necessary) in the form of sand added. The ferrous oxide then unites with the silica forming a fusible slag of ferrous silicate and the molten cuprous sulphide settles to the bottom of the furnace. The impure sulphide, which is now very much richer in copper, still contains some sulphide of iron and has approximately the same composition as pure copper pyrites. It is known as **copper matte** or **coarse metal**.

The coarse metal is subjected to a very similar treatment by which the rest of the iron is removed and a nearly pure cuprous sulphide, known as **fine metal**, is left. The fine metal is heated in lumps in a special furnace with free access of air and is thus slowly oxidised to cuprous oxide without undergoing fusion. The furnace is so arranged that as soon as sufficient oxide has been formed, the air supply can be cut off and the temperature raised sufficiently high to melt the mixed oxide and sulphide when a violent reaction takes place, the sulphur of the sulphide combining with oxygen from the oxide, sulphur dioxide escapes and metallic copper is left. The crude metal is known at this stage as **blister copper** and the reaction by which it is produced is :—



Blister copper, so called because of its appearance, caused by the escape of sulphur dioxide on solidification, contains some 2 or 3 per cent. of impurities of which arsenic is the chief. It is further refined by being melted in lots of 8-10 tons in a stream of air. Sulphur and arsenic are thereby oxidised to sulphur dioxide and arsenic trioxide respectively, and these volatile oxides are driven off, whilst iron, tin and lead are also converted into their oxides, which separate together with some cupric oxide as a scum or slag. This slag can be worked up in the second fusion described above. The chief impurity remaining in the copper is cuprous oxide (Cu_2O), which dissolves in molten copper and forms an eutectic with it containing 3·4 per cent. of the oxide. This eutectic crystallises out at a temperature of 1065°C ., that is, after most of the copper has crystallised; it has the effect of making the metal brittle and causing a considerable lowering of its electrical conductivity. It is therefore highly important that the

amount of cuprous oxide present should be reduced to the lowest minimum (Fig. 14). To accomplish this, the purified metal is melted under a thin layer of anthracite and the whole mass stirred with a heavy pole of green birch wood. In this poling process, reducing gases are evolved which reduce the oxide to the metal, and they have also the effect of so thoroughly mixing the metal that uniformity of the product is ensured. When the operation is carried out successfully, copper of 99.5 per cent. purity is obtained.

Electrolytic Refining.—For many purposes, especially in the electrical industry, copper of the very highest degree of purity is required. This is obtained by a process of electrolysis. The copper to be purified is cast into oblong plates about an inch thick and five square feet in area. The plates are clamped parallel to one another and about four inches apart, forming a large compound anode. This anode is

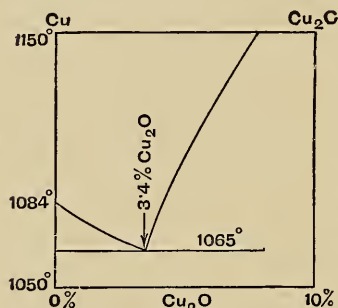


FIG. 14.—FREEZING-POINT DIAGRAM FOR COPPER AND CUPROUS OXIDE.

immersed in a solution of copper sulphate acidified with sulphuric acid contained in a lead-lined wooden vat. The cathode or negative pole consists of a similar arrangement of thin (0.1 inch) pure copper plates which are clamped together in the same manner and inserted between the anode plates without touching them. On passing the electric current (about 50 amperes for the size of plate indicated) copper is dissolved from the anodes and deposited on the cathodes, from which it is easily detached when of suitable thickness. Iron or nickel which may be present in the original copper pass into solution and are not deposited as long as sufficient copper sulphate is present. Other metals which formed impurities in the original metal are deposited either in the metallic state, *e.g.* silver and gold, or as insoluble salts, *e.g.* lead as lead sulphate, or as insoluble basic salts, *e.g.* antimony and bismuth, and form what is known as anode slime. This slime is collected, melted into ingots, and treated with sulphuric acid. From the sulphuric acid solution silver may be precipitated with copper or iron, whilst the insoluble residue of gold is melted and cast into ingots. This is a valuable source of silver and gold. The refined copper obtained on the cathode is of 99.9 to 99.98 per cent. purity; the only measurable impurities are traces of iron, antimony and cuprous oxide.

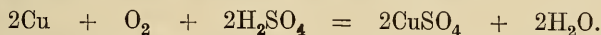
Properties of Copper.—Pure copper is a lustrous red metal. The density of electrolytic copper is 8.945, its melting point is 1083° C., and its coefficient of linear expansion for ordinary temperatures is 0.0000171. The metal is soft and tough, and resembles aluminium in many of its mechanical properties. Cast copper has a tensile

strength of 10 tons per sq. in. (16 kg. per sq. mm.) and this can be approximately doubled by rolling the cast metal into sheets. It is very malleable and can be hammered or rolled into thin sheets, provided it is frequently annealed during the process. On account of its high tenacity, copper can be drawn into very thin wire. In electrical conductivity, copper ranks only below silver, having a value of 95 if that of silver be reckoned as 100, and hence the importance of copper in the electrical industry.

Copper shows a great readiness to blend with other metals, forming homogeneous liquid alloys and solid solutions. It forms solid solutions in all proportions with nickel, which greatly increases the electrical resistance of the copper. **Constantan** is a copper-nickel alloy containing about 40 per cent. of nickel, and is remarkable on account of its low temperature coefficient. Copper also forms solid solutions with palladium, platinum, and gold. The alloys of copper with tin (bronzes) and with zinc (brasses) are described later (pages 81, 82). The fact that cuprous oxide dissolves in molten copper and forms an eutectic with it, and the effect of this on the mechanical and electrical properties of the metal, have already been pointed out. Similarly, cuprous sulphide (Cu_2S), cuprous phosphide (Cu_3P), cuprous arsenide (Cu_3As), cuprous antimonide (Cu_3Sb), cuprous silicide (Cu_3Si), and the compounds of copper with magnesium, behave in a similar manner, and have a similar effect on the properties of copper. For this reason the importance of freeing copper in its purification from non-metallic and metallic impurities cannot be too strongly emphasized.

Copper remains unchanged in pure, dry air at ordinary temperatures, but the metal becomes covered with cupric oxide (CuO), or black scale, when heated below its melting-point in air or oxygen. When the metal is heated above its melting-point, the red cuprous oxide (Cu_2O) is formed, and this is soluble in the liquid metal. In damp air, copper is soon tarnished owing to the formation of a basic carbonate, similar in composition to malachite, the naturally occurring basic carbonate. In town air, the metal is rapidly tarnished by the formation of a film of cupric sulphide (CuS).

In the absence of air or oxygen, copper is unaffected by dilute sulphuric acid even on boiling, but in the presence of oxygen the copper gradually dissolves, forming copper sulphate,

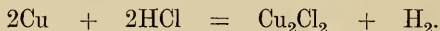


Copper is rapidly dissolved by hot concentrated sulphuric acid, forming copper sulphate and liberating sulphur dioxide,



Similarly, in the absence of air, copper is not affected by hydrochloric acid at ordinary temperatures, but finely divided copper

when heated with concentrated hydrochloric acid forms the white cuprous chloride and slowly liberates hydrogen,



Ordinary dilute nitric acid is the best solvent for copper. It dissolves the metal rapidly, forming the soluble copper nitrate $[\text{Cu}(\text{NO}_3)_2]$, and liberating oxides of nitrogen. Even many of the comparatively weak organic acids attack copper slowly in the presence of air or oxygen, forming basic salts; thus acetic acid under these conditions forms the well-known **verdigris**, which is basic copper acetate. Ammonia in the presence of air slowly dissolves copper, forming a dark blue solution, but the other alkalies have no action on the metal.

On account of its chemical properties, pure copper cannot be used in the mouth, but it forms a valuable constituent of gold plate and German silver, which are important materials in prosthetic dentistry. At the same time, it is obvious, that a material possessing such valuable mechanical and electrical properties finds innumerable applications in the laboratory. Copper wire of various diameters is used for many purposes, and copper foil has been recommended as a lining beneath gold fillings. Copper foil is also used for absorbing surplus mercury from the surface of amalgam fillings. Various vessels in the laboratory are made of copper and employed for such purposes as its chemical properties permit. The soldering-bit used in working soft solder is made of copper on account of its heat-retaining properties.

The coating of iron, steel, and other base-metal articles with pure copper preparatory to nickel- or silver-plating is effected by a process analogous to electro-gilding, the article forming the cathode or negative pole and a plate of pure copper the anode, the electrolyte being a solution of potassium cuprocyanide $(\text{KCuC}_2\text{N}_2)$.¹ In copper-plating, as in silver-plating, it is essential that the surface to be plated should be chemically clean, otherwise the metal will not adhere perfectly. The article having been polished, grease is removed by washing with a suitable organic solvent, and then in a hot 10 per cent. solution of sodium hydroxide. The article is rinsed in water, and then dipped for a moment in a 10-per cent. solution of sulphuric acid, rinsed thoroughly in water, and transferred straight away to the plating bath. It is advisable not to touch the surface of the article with the fingers, so as to avoid the slightest greasy contamination. The layer of copper deposited prior to silver- or nickel-plating should be as thin as possible.

If the surface of the article to be plated is not specially cleaned, and

¹ Copper sulphate $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$, 8 grams; pure potassium cyanide (KCN), 10 grams; concentrated ammonia solution, 40 drops—the whole being made up to 100 c.c. with water. The ammonia is added last, after the formation of the cuprocyanide.

a fairly thick layer of copper is deposited, this may afterwards be detached as in the electrolytic refining of copper. A cast is thus obtained which produces every irregularity of the original surface, and is known as **electrotype**. Impressions taken in gutta-percha or plaster may thus serve for the production of models in copper. If plaster be employed, the impression must be well dried and soaked in paraffin wax before immersion, otherwise it will be rapidly disintegrated by the acid solution to be employed in this case; gutta-percha, either alone or melted with half its weight of lard, is preferable. A conducting surface is given to the cast by coating it with graphite or copper powder (or bronze powder), and when suspended by a copper wire, it is made the cathode in a solution of copper sulphate acidified with sulphuric acid;¹ the anode consists of a plate of pure copper. Depressed parts of the surface receive less deposit than the raised parts, and hence it is advisable that the current density should be raised locally by auxiliary branch anodes of copper wire terminating just opposite such depressions, and as close to them as possible without actually being in contact.

Alloys of Copper.—The alloys containing silver and gold have been described under those two metals. Other alloys of copper with manganese, lead, and antimony have been studied, and some of them put to important technical uses. From many points of view, however, the most important of the copper alloys are those of the three series—copper-tin, copper-zinc, and copper-aluminium.

Copper-tin Alloys, which constitute the various varieties of bronze, have been carefully investigated, chiefly by Heycock and Neville. The alloys show considerable resemblances in their constitution to those of copper and zinc (see below). Copper and tin form two principal series of solid solutions, known as the α - and the β -series, and a white brittle compound, Cu_3Sn , which contains approximately 61.6 per cent. of copper. The formation of this compound limits the amount of tin which can be usefully added to copper. The alloys which consist of solid solutions of the β -series differ from those of the α -series not only in their higher tin content, but also in being much more brittle. Solid solutions of the α -series contain up to 13 per cent. of tin, and alloys containing from 13 to 25 per cent. of tin consist of both α - and β -crystals. The brittleness of the β -series is probably due to the fact that the compound Cu_3Sn readily separates from them. Most of the commercial bronzes contain less than 25 per cent. of tin, and contain crystals of the α -series which separate first. Generally, the strength of the alloy increases and its ductility diminishes as the proportion of tin increases. **Speculum metal**, which is a white alloy of copper and tin, is used for making mirrors,

¹ Copper sulphate, 86 grams, dissolved in 300 c.c. of water, then 15 c.c. of concentrated sulphuric acid cautiously added, and the whole made up to 600 c.c. with water. A current density of about 0.02 ampère per square inch is best.

since it takes a high polish and does not readily tarnish. It contains about 33 per cent. of tin, and it consists of crystals of the β -series of solid solutions.

Gun metal is a soft bronze which contains 8-12 per cent. of tin. **Bell metal**, the tin content of which is much higher than that of gun metal, viz. 12 to 24 per cent., is much harder, since it consists of crystals of solid solutions of the α -series, which separate primarily with those of the β -series. **Phosphor bronze**, which is used extensively as a substitute for steel where rusting and corrosion must be reduced to the minimum, e.g., for bearings, pump-linings, valves, and taps, is one of the strongest of the non-ferrous alloys. Its composition varies considerably, and it contains varying small quantities of lead and phosphorus in addition to lead and tin.

Brass is the general name given to the alloys of copper and zinc. Copper forms a compound with zinc, having the composition Cu_2Zn_3 , containing about 39 per cent. of copper. The compound is white, and all alloys containing more than about 60 per cent. of zinc are described as **white metal**. The formation of the compound, Cu_2Zn_3 , limits the proportion of zinc which can be usefully alloyed with copper. The alloys of copper and zinc show many similarities to those of copper and tin. Thus, apart from the formation of a compound, copper and zinc form different types of solid solutions known as the α -, β -, and γ -series respectively. Crystals of the solid solutions of the α -series are isomorphous with those of copper, and contain generally up to 30 per cent. of zinc, and the percentage of zinc can be slightly increased by low temperature annealing. Crystals of the solid solutions of the β -series contain from about 36 to 60 per cent. of zinc, and appear to be isomorphous with the crystals of the compound Cu_2Zn_3 . By annealing at low temperatures the range of composition of the β -series is contracted to about 48 per cent. of zinc, and then the excess of the zinc separates in the γ -form as the compound.

The difference in mechanical properties of the alloys of the α - and β -series is illustrated by the two chief brasses, viz., ordinary or **cart-ridge brass** and **Muntz metal**. The former contains about 30 per cent. of zinc, and, according to what has been pointed out above, represents the extreme limit of the solubility of zinc in copper to form solid solutions of the α -series at the temperature of solidification. It is much more brittle than copper when hot, but at ordinary temperatures it is almost as plastic as copper, and can therefore be rolled or drawn without cracking. On the other hand, Muntz metal, which contains 40 per cent. of zinc, crystallises in the β -series, and it is not only plastic when hot but also when cold. The alloy is much harder than ordinary brass, and its resistance to corrosion has rendered its use possible for marine purposes.

The addition of nickel to copper-zinc alloys gives rise to a series of very useful alloys known as **German silver**. German silver, which

may be regarded as brass in which part of the copper has been replaced by nickel, is especially useful in dentistry on account of its incorrodibility in the mouth.

With aluminium, copper forms a series of alloys which again show many points of similarity to the bronzes and the brasses. Apart from the formation of a compound, CuAl_2 , the alloys form a series of solid solutions. The series of alloys containing up to 10 per cent. of aluminium are known as **aluminium bronzes**, and, apart from possessing very high tensile strength, are very much less corrodible than either of the constituent metals. The alloy containing 10 per cent. of aluminium is of pale golden colour, melts at 930°C ., and gives very good castings, although with considerable shrinkage. It is much more resistant to acids than ordinary bronze, and is not affected by hydrogen sulphide. The alloy containing 5 per cent. of aluminium has been recommended for metallic sutures in place of silver wire, and it is far superior to silver in tenacity, pliability, and antiseptic properties, and is non-irritant. These properties also render the ordinary aluminium bronze, containing 10 per cent. aluminium, suitable for denture bases, and for such it has been employed with good results. Surfaces of aluminium bronze may be united by means of hard or soft solders. In the former case a good gold solder is employed, using borax as a flux. For soft soldering, the parts are first cleaned, and then coppered by immersion in a strong solution of copper sulphate, the two parts being connected with a soft iron rod. By this means a copper surface is produced, which can be brightened and tinned in the usual way with a soldering bit, using zinc chloride as a flux.

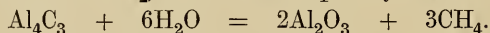
CHAPTER VI

ALUMINIUM AND ITS USES IN DENTISTRY

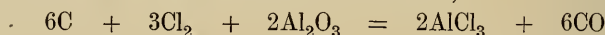
ALUMINIUM—Al. (Atomic Weight = 27.1); Valency, 3.

Occurrence.—Aluminium is the third most abundant element contained in the earth's crust. It is an essential constituent of all clays which are disintegration products of the various varieties of mica, these latter being complex silicates of aluminium and, generally, potassium and magnesium. Other naturally occurring complex silicates are the felspars which contain besides aluminium chiefly sodium, potassium and calcium. The source from which aluminium is extracted is the oxide alumina, Al_2O_3 . This occurs in the hydrated form together with iron oxide, Fe_2O_3 , as **laterite**, found in large deposits in India, especially in the South, and besides being used as a source of aluminium is also used as a crude building material. A fairly pure hydrated alumina occurs as **bauxite**, first found at Baux near Arles, in France, and it is from this that the greater proportion of the aluminium is produced. Corundum or emery is an impure crystalline variety of anhydrous alumina and the better forms of it show a great variety of colours probably due to the presence of ferric oxide, Fe_2O_3 , and also to traces of chromium. Such crystalline specimens are often very beautiful and have great value as gem stones, *e.g.* ruby (red), sapphire (deep blue to lilac colour), emerald (green), and amethyst (purple). Another important ore containing aluminium is the sodium aluminium fluoride cryolite Na_3AlF_6 , found chiefly in Greenland. Cryolite is used along with alumina (purified bauxite) in the manufacture of aluminium.

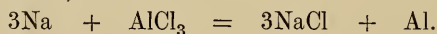
Extraction.—Aluminium combines with oxygen and other non-metallic elements with very great readiness, and the ordinary processes used in metallurgy cannot be employed for the extraction of the metal. When aluminium oxide is heated with carbon in the electric furnace, aluminium carbide, Al_4C_3 , is produced. This carbide is interesting in that it produces methane, and not acetylene (compare calcium carbide, CaC_2), when acted upon by water,



Formerly, the only method used in isolating aluminium was to reduce aluminium chloride, AlCl_3 , prepared by the action of chlorine on a heated mixture of aluminium oxide and charcoal,



by means of sodium,



The metal obtained by this method was often contaminated with sodium and thereby rendered particularly susceptible to corrosion.

Aluminium is now prepared by the electrolysis of a fused mixture of cryolite and aluminium oxide (bauxite, carefully purified and free from oxide of iron). The electrolysis is carried out in an iron box lined with carbon, and this is made the cathode, whilst a number of stout carbon rods clamped together serves as the anode. The cryolite is fused by the heat generated by the passage of the electric

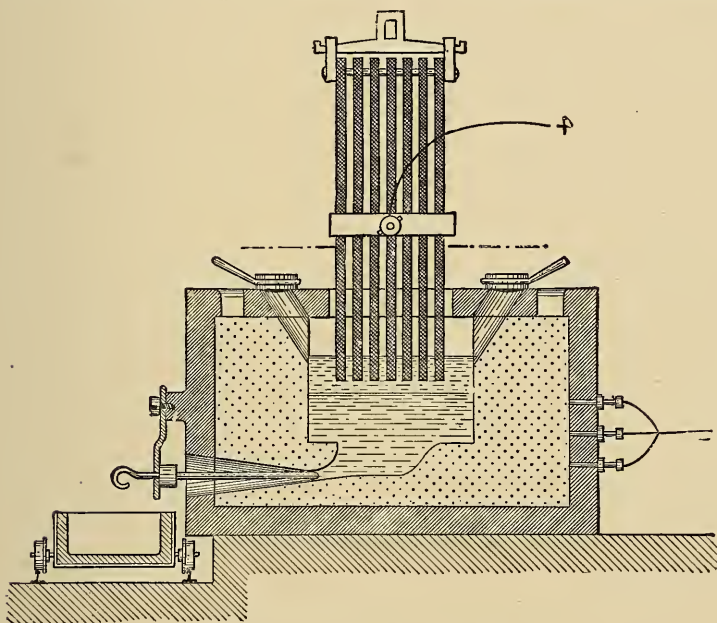


FIG. 15.—MANUFACTURE OF ALUMINIUM.

current and the oxide is added. The voltage between the electrodes is about 6 volts and the electrical resistance generates sufficient heat to keep the electrolyte molten. As the alumina is decomposed a fresh amount is added so as to keep the concentration constant. The oxide may be regarded as being simply decomposed by the current as follows :—



The aluminium sinks to the bottom and can be drawn off, while the oxygen burns up the carbon anodes (Fig. 15).

Since aluminium forms compounds so readily with the non-metallic elements, there is considerable difficulty in purifying the metal when once it is isolated, and it is therefore important that the metal isolated by electrolysis should be obtained in such a state as not

to require further purification. This almost entirely depends on the quality of the alumina used. The bauxite may be roasted to drive off all water and then heated in the electric furnace with just sufficient carbon to reduce all the iron oxide present. The purest alumina, however, is obtained by digesting the roasted bauxite with strong sodium hydroxide solution. This dissolves all the aluminium oxide and most of the silica present. The aluminium oxide is converted into the soluble sodium aluminate,

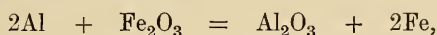


and the oxide of iron is left unattacked. The liquid is diluted considerably and filtered and the filtrate stirred with a small quantity of pure alumina (from a previous operation) when about three-quarters of the alumina is precipitated as the gelatinous hydroxide, $\text{Al}(\text{OH})_3$. This reaction, which has replaced the older method of precipitation by means of carbon dioxide, is difficult to explain chemically, and it is convenient, since the caustic soda solution can be used again after concentration. The gelatinous hydroxide is collected by means of a filter press, thoroughly washed, dried, and finally converted into the anhydrous oxide by roasting to a bright red heat. Such oxide should now be free not only from iron but also from silicon.

Properties and Uses of Aluminium.—Aluminium is a silver-white metal which melts at 659°C . It is remarkable for its lightness (density=2.7), high specific heat (0.219 at 15°C .), and high tensile strength. While the tensile strength of cast aluminium is only slightly more than half that of cast copper, for equal weights, aluminium is nearly twice as strong. Again, the electrical conductivity of aluminium is about 60 per cent. of that of copper (aluminium ranks third in the order of conductivities of the metals), but for equal weights of the two metals the conductivity of aluminium is twice as great. Thus, it appears that aluminium might if necessary replace copper on account of its mechanical and electrical properties, especially in the latter case in the construction of electrical cables when the latter do not require insulation.

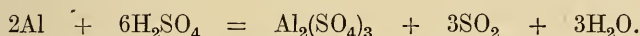
Although aluminium has a very great affinity for oxygen, and its oxide is not reduced either by hydrogen or carbon monoxide, the metal retains a dull lustre in air and is not at all easily ignited. This is probably due to the surface of the metal being coated by a thin but impermeable layer of the oxide. When the surface of a piece of aluminium is amalgamated with mercury, the metal is rapidly oxidised in air and becomes distinctly warm. The oxide appears as feathery growths, and its rapid formation is probably due to the mercury breaking up the otherwise permanent film of oxide on the surface. The great affinity of aluminium for oxygen is indicated by the large heat of formation of the oxide. This is applied in the Goldschmidt process for the preparation of metals such as chromium from their

oxides. Chromium oxide, for example, cannot be reduced to the metal by means of carbon, but it can be reduced by means of aluminium under similar conditions as obtain in the **thermite** process for welding iron. In this process, aluminium powder and iron oxide, Fe_2O_3 , are mixed together and covered with a small quantity of a mixture of aluminium powder and barium peroxide. A fuse of magnesium is placed in the mixture, and when the magnesium is well alight the ignition of the mixture starts and proceeds rapidly. The oxide of iron is reduced to the metal,

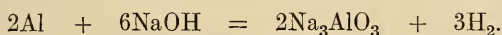


and the temperature is so high that the iron is fused. Tramway rails can be welded together *in situ* by this method.

Aluminium also combines directly when heated strongly with chlorine, sulphur, and even nitrogen, forming the chloride, AlCl_3 , the sulphide, Al_2S_3 , and the nitride, AlN , respectively. Nitric acid, whether strong or dilute, has but very slight action on aluminium, but the metal is rapidly dissolved by hot concentrated hydrochloric acid, forming a solution of the chloride and liberating hydrogen. Aluminium is also slowly attacked by dilute sulphuric acid when hydrogen is liberated, but the hot concentrated acid rapidly dissolves it, with the formation of aluminium sulphate and evolution of sulphur dioxide,



Like zinc, aluminium is rapidly dissolved by hot solutions of sodium and potassium hydroxides. Hydrogen is evolved and soluble aluminates are formed,



Aluminium has a considerable action on many salts in solution. It precipitates silver slowly from a neutral or feebly acid solution of silver nitrate, while silver is rapidly precipitated as a crystalline powder from an ammoniacal solution of silver chloride. Mercury salts are easily decomposed by aluminium and aluminium amalgam is formed.

Aluminium is largely used in the manufacture of cooking utensils. Its use for this purpose is recommended in preference to tin and copper on account of the relatively harmless nature of aluminium compounds should these be produced in small quantities during the cooking of food. The resistance of aluminium to nitric acid renders the metal particularly valuable for the construction of certain types of chemical plant. On account of the action of alkalies upon it, aluminium cannot be used with alkaline liquids.

Aluminium in Dental Practice.—In the past, the use of aluminium for making prosthetic appliances has proved somewhat disappointing. Although not so light as vulcanite, its lightness, malleability, tenacity,

high specific heat, and its resistance to the action of hydrogen sulphide are properties which obviously render aluminium particularly suitable for the construction of denture plates. These valuable properties were formerly counterbalanced by the difficulties which arose through the corrodibility of the metal by the oral fluids and by the difficulties of soldering. This corrosion was undoubtedly due to the presence of impurities in the metal itself, and to those due to contamination from the dies and counter-dies used in the construction of the base plates for the denture, especially when no precautions were taken, such as the use of tissue paper or silk in swaging. These difficulties have now been overcome. Aluminium is now made almost chemically pure by the electrolytic process. The risk of contamination of aluminium by the use of dies and counter-dies has been eliminated by casting, instead of swaging, the plate. Aluminium is electro-positive to all other metals used in the mouth, and this, together with its lack of rigidity and the difficulties of soldering, renders it inadvisable for use in the construction of partial dentures. It is more suitable for use in the construction of complete upper dentures where a combined metal and vulcanite case is required, and the retaining factors in the mouth are such that a gold base plate cannot be employed on account of its weight.

Construction of an Aluminium Plate.—The impression having been taken in the usual manner, the model should be cast in a mixture of plaster of Paris and Portland cement, so as to obtain a hard model. In making the wax model for a cast aluminium base plate, it is necessary to provide tags for the attachment of the vulcanite holding the teeth so as to eliminate the necessity of soldering the tags, or, as was formerly the case, of punching holes in the plate. The metal is melted without a flux in a plumbago crucible under a layer of charcoal so as to prevent oxidation during the melting. More metal is fused than is required for the making of the plate. Before casting, it is essential that the ring and investment should be red hot, and when the aluminium is fused the charcoal is blown off the surface and the molten metal poured on to the mould and cast under a pressure of about 20 lbs. Any aluminium oxide which may have formed will have risen to the surface, and, since an excess of the metal has been employed, the oxide will be prevented from entering the mould. Aluminium contracts during solidification to a greater extent than gold, and it is therefore necessary to replace the cast base plate on the hard plaster model and swage it into position by means of a shot or plasticene swager. Since the tags have been cast with the plate, it is only necessary to attach the teeth by means of vulcanite; the rim of vulcanite also increases the rigidity of the plate. Aluminium cannot be cast directly on to the teeth on account of the contraction of the metal giving rise to minute fractures in the porcelain. These fractures may not be visible at first, but soon become obvious when the plate has been worn. A

process for the gilding of aluminium plates is greatly needed, but has yet to be discovered.

Other Uses of Aluminium.—Aluminium is now used extensively in the making of dental instruments, especially for those which require large handles, such as elevators, enamel chisels, scalers, etc. It is, however, not an easy metal to work, since its peculiar toughness causes it to stick to the tools, rendering lathe work and special polishing somewhat unsatisfactory.

Impression trays struck from sheet aluminium possess the great advantage of considerable flexibility, which enables them to be adapted to all irregularities of the dental arch. In constructing these trays in the laboratory, the handles are most conveniently attached by riveting.

The alloys of aluminium with copper have already been mentioned (page 83). These alloys, like aluminium itself, are employed in the construction of base plates for dentures.¹

Solders for Aluminium.—It has been indicated that there is considerable difficulty in uniting two pieces of aluminium by soldering. The impracticability of using an ordinary flux, such as borax (on account of its acting as a relatively strong alkali), makes it difficult to maintain a clean surface, owing to the rapidity with which aluminium oxidises at the soldering temperature. Various hard and soft solders have been devised, but none have proved thoroughly satisfactory for dental purposes.

Of the compounds of aluminium, the silicates are of the highest importance in dental practice. They form the chief ingredients of porcelain, used in the manufacture of artificial teeth, etc., and they are the basis of the powder in the silicate cements which are so extensively used in conservative work, on account of their translucency. The aluminium silicates are referred to in the present work under "Porcelain" and "Dental Cements" respectively.

¹ Many other aluminium alloys are of very considerable importance. The alloy of aluminium, with 2 to 10 per cent. of magnesium, and known as **magnalium**, is lighter than aluminium, and equal in strength and workability to brass, and is said to be resistant to atmospheric corrosion. **Duralumin** is a very important alloy, containing about 4 per cent. of copper, and smaller quantities of manganese and magnesium. For an account of these and other aluminium alloys see the Ninth and Tenth Reports of the Alloys Research Committee of the Institute of Mechanical Engineers.

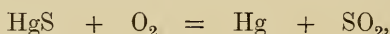
CHAPTER VII

MERCURY: AMALGAMS: VERMILION

MERCURY—Hg. (Atomic Weight=200·0); Valency, 1 and 2.

Occurrence.—Mercury is found as the metal in small quantities, but the most important source of the metal is the sulphide (HgS), which occurs as the mineral **cinnabar**, which, when massive, has a rich vermilion colour, and is highly crystalline. This ore is found in Austria, Italy, and in California, but the most important cinnabar mine is at Almaden in Spain.

Extraction of Mercury.—The metallurgy of mercury is comparatively simple. It depends on the following reaction:—



and consists in heating the ore by itself in a reverberatory furnace in the presence of excess of air or in a small blast furnace heated externally. The mercury is volatilized, and condensed in an elaborate condensing plant. Ores rich in mercury are usually mixed with either lime or iron before being heated. These substances prevent the carrying away of mercury vapour in the current of air. Under the circumstances the following reactions take place:—



Purification of Mercury.—In dentistry, it is specially important that pure mercury should be used. On account of the fact that mercury readily dissolves many of the metals, it is very liable to become contaminated. Crude mercury may be purified by mixing it with a little lime or iron filings, and distilling it from an iron retort. The lime and iron decompose compounds of mercury, and the distilled metal is obtained free from impurities less volatile than itself. Mercury can also be freed from base metals by dropping it in the form of small globules down a long column of 5 per cent. nitric acid, when the base metals go into solution. It may be necessary to repeat the process several times, and the mercury can be washed free from acid with pure water, separated from the latter, and dried carefully. The most effective method for the purification of mercury is by distillation in a vacuum. Various types of apparatus have been described for this purpose, in which the distilled mercury acts as a barometric column (Fig. 16). Another method which is recommended, consists

in heating the metal at 150°C . in a flask, while passing a current of dust-free air through it by means of a glass tube extending about 1 cm. below the surface of the metal. After several hours the metal is filtered from the scum, and again treated by the same method. The process is repeated until no more scum forms, after which the filtered metal is distilled under reduced pressure in an ordinary fractionating flask.

Properties of Mercury.—Mercury is a silver-white metal, and, apart from being the only metal liquid at ordinary temperatures, is also the heaviest liquid known under these conditions. Its density is 13.595 at 0°C . It freezes at -38.85°C ., and boils at 357.25°C . It has a definite but small vapour pressure (0.00069 mm. at 15°C .). Mercury contracts considerably on solidification, and the solid metal is crystalline, and possesses other metallic properties such as ductility and malleability.

Pure mercury is not affected by air or oxygen, but when contaminated with base metals, especially zinc and lead, it becomes superficially oxidised and coated with a grey film. By prolonged heating at its boiling point in air or oxygen, it combines with oxygen, forming the red mercuric oxide (HgO), and this gives up its oxygen when heated at a slightly higher temperature. Ozone rapidly oxidises mercury at ordinary temperatures. Dilute hydrochloric and sulphuric acid do not dissolve mercury. It is readily dissolved by moderately concentrated nitric acid, when mercuric nitrate is formed, and also by hot concentrated sulphuric acid, when sulphur dioxide is evolved and mercuric sulphate is produced:—



Mercury combines directly with chlorine, bromine, and iodine forming mercurous or mercuric compounds, according to the relative amounts

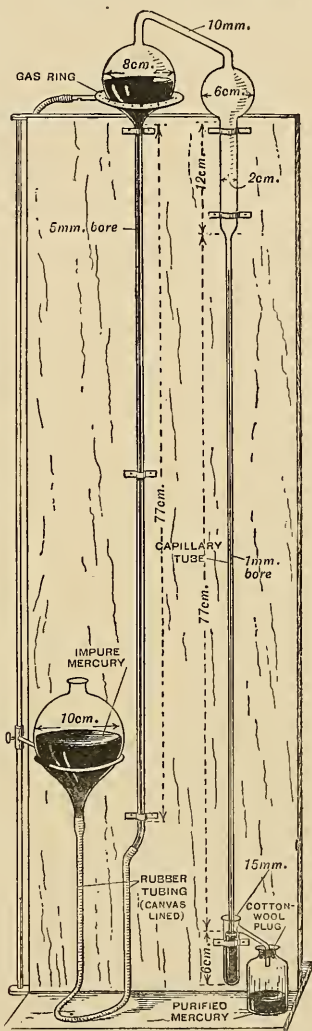


FIG. 16—APPARATUS FOR THE PURIFICATION OF MERCURY BY DISTILLATION.

of mercury and halogen interacting. Mercury is also acted upon by hydrogen sulphide, when mercuric sulphide is produced.

AMALGAMS

Amalgams are solutions of other metals in mercury, *i.e.* they are alloys in which one of the constituent metals is mercury. The constitution of amalgams and the methods of investigation therefore are precisely the same as those of alloys.

Amalgams are usually prepared by simply dissolving metals in mercury either at the ordinary temperature or on heating. Mercury dissolves most of the metals under these circumstances, but it does not dissolve iron and the metals closely related to it. Mercury is therefore conveniently packed in iron bottles. Other methods of preparing amalgams occasionally employed are (*a*) by the addition of mercury to a solution of the salt of a metal which mercury is capable of replacing, (*b*) by the electrolysis of a solution of the salt of the metal, the negative pole or cathode dipping into a globule of mercury.

The fact that many amalgams are pasty when prepared by the ordinary method, and then harden on standing, led to their use as conservative materials for filling teeth after the degraded enamel and dentine have been removed, and the cavity suitably cleansed and sterilised. The qualities of an ideal filling material have already been discussed, and, after gold, amalgams are the most generally employed, and are useful substances for this purpose. Before discussing the modern dental amalgams, it is desirable to consider the nature and properties of some simple amalgams which are prepared by the direct method.

Sodium and **potassium** both dissolve in mercury readily with evolution of heat. Several compounds have been proved to exist in both cases, *e.g.* NaHg_4 , NaHg_2 , NaHg , KHg_2 , KHg , being the simplest ones. Sodium amalgam finds extensive use in chemistry as a reducing agent in alkaline solution. The amalgams of low sodium content are liquid, and probably contain one or more compounds dissolved in excess of mercury. The solid sodium and potassium amalgams are highly crystalline.

Aluminium does not readily dissolve in mercury at ordinary temperatures, but on heating, and especially when finely divided, it goes into solution fairly readily. When mercury is rubbed on the surface of a piece of aluminium foil, which has been moistened with a little sodium hydroxide solution, amalgamation takes place, and the surface exposed to the air becomes covered rapidly with aluminium oxide, which is formed with considerable evolution of heat. The characteristic fungus-like production of aluminium oxide on the surface of aluminium, especially when this has been previously moistened with a little dilute hydrochloric acid, which has been rubbed with a little mercury, has

already been described. The amalgamation, even to a small extent, of aluminium increases the rate of oxidation of the latter metal very considerably, and this has been urged as an argument against the use of aluminium dentures in mouths which contain amalgam fillings. The writer, however, is of the opinion that if the amalgam filling has been properly made and inserted, it will not contain any excess of mercury as such, and therefore the aluminium of the denture will not be affected from this cause.

Copper when finely divided, and especially in the presence of a small quantity of mercuric nitrate solution, amalgamates fairly readily with mercury by simply rubbing the two metals together. The resulting pasty product can be separated from the excess of mercury by expressing it through chamois leather. After washing with hot water and drying, it is quite hard, but becomes soft on heating. Care should, however, be taken to avoid loss of mercury by volatilization. The resulting amalgam, known as **Sullivan's amalgam**, contains from about 25 to 35 per cent. of copper, and is famous for its edge strength, and especially for the fact that it hardens on cooling, with practically no change in volume. It has the disadvantage that it darkens on account of oxidation, and the action of hydrogen sulphide, the black stain usually spreading to the tooth substance, although this can to a certain extent be avoided by lining the cavity, as is usually done, with the adhesive zinc oxyphosphate cement before inserting the amalgam. The earliest amalgams to be used for filling purposes consisted of filings of silver coins mixed to a paste with mercury. These fillings fell out of use largely on account of the same kind of staining, although it is claimed by some that the presence of copper actually arrests further development of caries.

Cadmium dissolves readily in warm mercury, and the two metals form two series of solid solutions, and the freezing-point curve shows a discontinuity. When warmed, the solid amalgam softens and hardens again on cooling. It was formerly used as a filling material, but its use has been abandoned on account of its turning yellow in the mouth, due to the action of hydrogen sulphide, which gives rise to yellow cadmium sulphide (CdS).

Lead, in the form of filings, readily amalgamates with mercury. The two metals form an eutectic which contains only a small quantity of lead and is liquid at the ordinary temperature, and lead dissolves about 31 per cent. of mercury, forming a solid solution. Amalgams containing more than about 4 per cent. of lead are solid at the ordinary temperature.

Zinc, especially when moistened with dilute hydrochloric acid, amalgamates with mercury at the ordinary temperature, and solution is readily effected when the mercury is heated. Zinc does not form a compound with mercury, but the two metals form an eutectic, containing about 2 per cent. of zinc, which freezes at -42.4°C. , and

amalgams containing more than about 5 per cent. of zinc are solid at ordinary temperatures. Zinc is a constituent of some modern dental amalgams.

Gold in a fine state of division readily dissolves in mercury at the ordinary temperature. This is made use of in the amalgamation process for the extraction of gold (p. 42). When the mercury has dissolved a certain amount of gold and the amalgam is squeezed through chamois leather, a pasty amalgam is left which contains most of the gold. The expressed mercury has been shown to contain a small amount of gold, and therefore the solution of gold in mercury behaves exactly like an aqueous solution of a salt. Compounds of gold and mercury have been stated to be capable of existence.

Palladium dissolves slowly in mercury, and palladium amalgam can also be obtained by the addition of mercury to a solution of a palladium salt. Palladium amalgam expands slightly on cooling, and has been used as a filling material. The amalgam is very durable, but as a filling it has the drawback that it becomes quite black. The stain, however, does not spread to the tooth substance.

Platinum, in the form of spongy platinum, dissolves in warm mercury, forming an amalgam with a silvery appearance. The amalgam is usually pasty, but it becomes more solid as the percentage of platinum increases, although it does not harden completely on standing.

Tin dissolves readily in mercury, even at the ordinary temperature. The two metals do not form a compound, and the constitution of the tin amalgams appears to be very similar to those of lead. The pasty amalgam, containing about 20 per cent. of mercury, is employed in the manufacture of mirrors. When a fluid amalgam is squeezed in chamois leather, the pasty mass remaining hardens after a few days. During the hardening a contraction in volume takes place, and this, apart from its slow hardening, renders tin amalgam as such unsuitable for filling purposes. Mercury is soluble in tin to a considerable extent, yielding soft crystals which are solid solutions of mercury in tin. On the other hand, tin is also soluble in mercury to an appreciable extent, and this solution does not solidify on standing. Modern dental amalgams always contain free tin, and it is important that the filling should not contain any excess of mercury, since, as pointed out above, free tin with an excess of mercury will not harden.

Silver dissolves slowly in mercury at the ordinary temperature, but much more rapidly on warming. According to the percentage of silver present, the amalgam is pasty or solid and crystalline. The solid amalgam is soluble in mercury, and the latter can be separated by expressing through chamois leather. Soft silver amalgam hardens slowly on standing, and during the process an increase in volume takes place. The use of silver amalgam as such for filling teeth has

been abandoned, partly on account of the expansion on hardening, and partly on account of the darkening of the amalgam due to the formation of silver sulphide, Ag_2S , by the action of hydrogen sulphide in the mouth. It has been pointed out (p. 73) that several compounds of silver and mercury are capable of existence. The compound Ag_3Hg_4 is the one most readily formed, and is a constituent of modern dental amalgams. It is also the chief constituent of the beautiful crystals which form the silver tree, "Arbor Dianæ," produced when mercury is allowed to stand in contact with a dilute solution of silver nitrate. Silver amalgams, containing probably the same compound, have been found in nature.

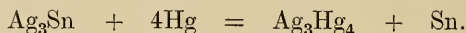
A brief consideration indicates that an amalgam to be used for filling purposes should at least possess the following properties :—

- (a) It should be soft enough to permit of ready insertion.
- (b) It should harden moderately fast after insertion, and should be capable of being burnished so as to present a smooth surface.
- (c) It should not expand or contract after insertion, but remain indefinitely as left by the operator.
- (d) It should not be brittle, but should be sufficiently hard to give permanently a good edge strength.
- (e) It should not be affected chemically by the oral fluids or conditions likely to pertain in the mouth. That is, it should not become discoloured or dissolve to form solutions of salts which may or may not be injurious.
- (f) Largely from an æsthetic point of view, it should possess a good colour, so as to be as inconspicuous as possible.

Of the amalgams already described, which contain only one metal besides mercury, not one fulfils all the above conditions. Copper amalgam and palladium amalgam possess useful properties as filling materials, but they do not withstand chemical action in the mouth. Probably the shrinkage on hardening is the greatest difficulty to overcome. The object of investigation has been chiefly to secure an amalgam containing such a mixture of metals that the shrinkage of one may be overcome by the expansion of another, and so secure a watertight plug. It is obvious that the use of a filling material which expands on hardening, *i.e.* after insertion, is attended by almost as great danger to the tooth as one that contracts during the same process.

Probably the rapid hardening accompanied by expansion of silver amalgam, and the slow hardening accompanied by contraction of tin amalgam led to the use of amalgams containing both silver and tin as filling material. All alloys used in the making of modern dental amalgams have both silver and tin as their chief constituents. The nature and properties of the silver-tin alloys have already been described (p. 72), and the properties of amalgams containing silver and

tin have been investigated by McBain and Joyner.¹ The alloys used in dental amalgams contain from about 40 to 70 per cent. of silver, and these alloys consist, as has been pointed out already, of the compound Ag_3Sn , and free tin. During the amalgamation with mercury the following chemical reaction takes place :—



The formation of the compound Ag_3Hg_4 , together with a knowledge of the properties of tin amalgam, indicate the proportion of mercury which should be added to the alloy. To avoid excess of mercury, which would form a permanently soft amalgam with the free tin either originally present or formed in the above reaction, only sufficient of the liquid metal which will combine with the silver present should be added. Knowing the silver content of the original alloy, the amount of mercury added should not be greater than that indicated by the formula of the compound, *i.e.* four atomic proportions to three atomic proportions of silver. The silver-tin amalgams containing a greater proportion of tin are softer and slower in setting than those containing a greater proportion of silver.

The quickest setting amalgam is made by mixing mercury with the silver-tin alloy of the composition of the compound Ag_3Sn , the quantity of mercury added being that indicated in the above equation. The use of this amalgam is, however, attended with certain disadvantages. It not only becomes discoloured, and therefore is acted upon to a certain extent by the oral fluids, but its shape after insertion is not permanent. With a view to overcoming these defects it has become the practice of the manufacturers of alloys to add other metals to the silver-tin alloys for use in the making of amalgam fillings. The metals generally added are gold, platinum, copper, and zinc. The presence of excess of tin in the alloy diminishes the tendency to discoloration, but it lowers the rate of setting, causes a shrinkage, and produces an amalgam of inferior edge strength. Gold added to the silver-tin alloys makes the amalgam easier to work ; it tends to increase the time of setting, diminishes the tendency to discoloration, reduces the shrinkage, and maintains a good edge strength. From the properties of platinum amalgam it would appear that platinum would confer undesirable properties on silver-tin alloy, to which it might be added for making a dental amalgam. This, indeed, is the case, since such an amalgam is slow in setting, shrinks on hardening, and is difficult to work. But when platinum is added to a silver-tin alloy which also contains gold, the amalgam produced after amalgamation with the requisite quantity of mercury sets quickly, is very hard, and retains its shape. Zinc is sometimes added to silver-tin alloys for producing filling amalgams. The zinc makes the amalgam whiter, and diminishes any tendency to discoloration.

¹ *Dental Cosmos*, June 1912.

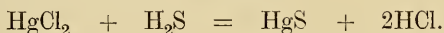
It does not diminish the edge strength, but it has a tendency to cause a change in form of the amalgam when it has set. In spite of the fact that copper amalgam has the disadvantage that it discolours very rapidly in the mouth, it has very useful properties, and the presence of small quantities of copper in silver-tin alloys to be used for amalgam fillings is to be recommended. It diminishes shrinkage, increases the edge strength, and facilitates the setting of the amalgam.

The alloys commonly supplied for the making of dental amalgams differ considerably in composition. In accordance with what has been pointed out above, platinum is never a constituent of an alloy to be used in an amalgam unless gold is present. Fletcher's platinum and gold alloy contains silver 43·35, tin 50·35, copper 1·65, gold 3·35, and platinum 1·30 per cent; and Tulloch's alloy, which is recommended as giving an amalgam which possesses a good edge strength and little, if any, shrinkage on hardening, contains silver 69·5, tin 25·5, gold 4, and zinc 1 per cent.

VERMILION

Vermilion, which is mercuric sulphide, HgS , is used for producing the red colour in vulcanite for denture plates. As a general rule the caoutchouc, sulphur, vermilion impregnated mixture contains about 33·3 per cent. by weight of the last-named substance.

It has been pointed out that the beautiful red crystalline mineral cinnabar is almost pure mercuric sulphide, and it is from this mineral that mercury is isolated. When hydrogen sulphide is passed into a solution of a mercuric salt, a black precipitate is obtained, which is the amorphous variety of mercuric sulphide,



This black amorphous mercuric sulphide on being heated in absence of air, sublimes, and then deposits the red crystalline form of the same compound, and this is known as vermilion.

Vermilion is prepared by either a dry or wet process. In the former, mercury and sulphur are heated together, and the black mercuric sulphide (often mixed with free mercury and free sulphur) results. This black mercuric sulphide, after being broken up, is heated in suitable vessels in such a manner that any sublimate is caught on a cover, which can be detached after the heating is finished. The sublimed mercuric sulphide obtained in such a manner is a very good variety of vermilion. The wet process for the production of vermilion consists essentially in the treatment of the black amorphous sulphide with sodium or potassium sulphide at a suitable temperature. It is believed that the production of the vermilion is due to the alternate formation and decomposition of a double sulphide of mercury and the alkali metal. In the case of potassium sulphide, the compound, $\text{K}_2\text{S} \cdot 5\text{HgS}$, is first produced, and is decomposed at about

45° C. with the deposition of the red crystalline mercuric sulphide, and the liberated potassium sulphide then combines with the readily attacked amorphous sulphide forming the same compound, which is again decomposed as before. By slightly varying the conditions of preparation, different qualities of vermilion are produced; but these different qualities of crystalline mercuric sulphide should not be confused with the different qualities of vermilion, which may be due to the crystalline mercuric sulphide being admixed with such substances as red lead, red oxide of iron (rouge), and even with gypsum (crystalline calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Like the black amorphous variety, the red crystalline mercuric sulphide, vermilion, is insoluble in hot concentrated nitric acid and in hydrochloric acid. It dissolves readily in aqua regia, and when heated in air is decomposed with the production of mercury and sulphur dioxide. It is also decomposed when heated with lime and such metals as copper, iron, and tin with the production of mercury and the sulphides of calcium and the other metals respectively (see above, p. 90).

CHAPTER VIII

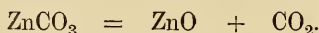
ZINC: COMPOUNDS OF ZINC: ALLOYS OF ZINC

ZINC—Zn. (Atomic Weight=65.37); Valency, 2.

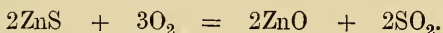
Occurrence.—The chief minerals from which zinc is obtained are the sulphide **zinc blende**, ZnS , which is found in England and in many districts in Europe, America, and in New South Wales, and the carbonate **calamine**, ZnCO_3 , found in many districts in Europe and in North America. Zinc also occurs in other minerals; **red zinc ore** is chiefly zinc oxide, ZnO , coloured by the manganese oxide present with it, and **gahnite** or zinc spinel is $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ or ZnAl_2O_4 .

Extraction of Zinc.—The extraction of zinc from the sulphide and carbonate depends on the conversion of these into zinc oxide, and the subsequent reduction of the oxide to the metal by heating with carbon.

The conversion of the carbonate (calamine) into the oxide is done by simple roasting,



Zinc sulphide is converted into zinc oxide by roasting in a regulated supply of air, care being taken to prevent the formation of zinc sulphate by oxidation,



The conversion of zinc sulphide into zinc oxide is conveniently carried out in the pyrites burners of a sulphuric acid plant, so that the sulphur dioxide can then be utilised for the manufacture of sulphuric acid by the contact process.

The reduction of the zinc oxide by means of carbon is carried out by heating the mixture of powdered oxide and powdered coke in a retort. The reaction which takes place is,

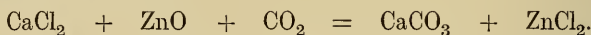


The retorts, usually not more than 5 feet in length and of about $2\frac{1}{2}$ cubic feet capacity, may be circular or elliptical in cross section, and are arranged in rows and tiers and heated by the same furnace. Each retort has its own condenser, which is fitted to the end of the retort. The colour of the carbon monoxide flame burning at the mouth of the clay adapter indicates that zinc is beginning to volatilise. The distillation is carried out at a temperature of about $1400^\circ \text{C}.$, and the temperature of the condenser has to be kept sufficiently high to prevent

the formation in it of solid particles of zinc dust. Under proper conditions the zinc distils over, and is collected in iron pots and subsequently cast in moulds.

This crude zinc or spelter contains about 98 per cent. of zinc, the chief impurities being lead (owing to presence of lead sulphide or galena in the original sulphide ore), cadmium, iron, and arsenic. Such crude zinc may be purified by remelting in a suitable vessel. Most of the lead separates by liquation, and the upper portion being zinc containing only about 1 per cent. of lead (see p. 72) can be separated off. The impurities remaining in the zinc can be got rid of by remelting with a suitable oxidising agent, such as sodium nitrate, when the lead and other metals are oxidised, and the oxides rising to the surface, separate as a scum. The arsenic is said to be eliminated by adding sodium to the zinc and heating for some hours.

Zinc of a purity of 99.96 per cent. is produced electrolytically by Messrs Brunner, Mond, Ltd. (Northwich). In this process the calcium chloride, which is a by-product in the Solvay process for the manufacture of sodium bicarbonate, is utilised. The calcium chloride solution is mixed with zinc oxide and carbon dioxide passed in at the same time. Zinc chloride, which goes into solution, and calcium carbonate, which is precipitated, are formed by a reaction which may be represented as follows,



The zinc chloride solution is then electrolysed, the cathode being iron discs mounted on a horizontally revolving axis, and the anode is made of carbon enclosed in a wooden frame. Chlorine is evolved at the anode and used for the manufacture of bleaching powder, and the zinc is stripped off the cathode, remelted, and cast into ingots.

Properties of Zinc.—Zinc is a bluish-white metal, the highly crystalline nature of which can be seen on breaking a rod or bar. The density of zinc is 7.1, and its melting-point and boiling-point are 419° C. and 918° C. respectively.

At the ordinary temperature zinc is brittle, while at about 120° C. it is malleable and ductile, and again at 200° C. it is so brittle that it can be easily powdered. It is possible that these changes in the behaviour of zinc may be due to the presence of impurities, but they may also be related to the changes in crystalline form which zinc undergoes. The changes in the crystalline form of zinc at 170° C. and at 340° C. appear undoubtedly to be related to the marked changes in its electrical conductivity at these temperatures, and zinc appears to be trimorphous like tin.

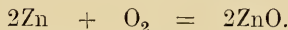
Pure zinc is not affected by water at the boiling-point, and it is but little affected by ordinary acids. Ordinary commercial zinc, on the other hand, dissolves rapidly in dilute sulphuric acid and in dilute

hydrochloric acid with evolution of hydrogen and the formation of the soluble sulphate and chloride respectively,

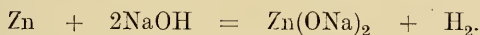


In nitric acid it dissolves with the formation of zinc nitrate, and the production of nitric oxide, nitrous oxide, nitrogen, and ammonia according to the conditions.

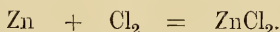
Zinc is not affected by dry and purified air or oxygen, but in the presence of moist air containing carbon dioxide it becomes coated with a white film of the oxide or carbonate which protects the metal from further corrosion. It is, however, much less easily corroded than iron, and is used for protecting iron from corrosion.¹ On being heated strongly in air, zinc burns with a greenish-white flame, and forms zinc oxide,



Like aluminium, zinc dissolves readily in boiling solutions of sodium and potassium hydroxides with evolution of hydrogen and the formation of soluble zincates,



Zinc combines directly when heated with chlorine, forming **zinc chloride**,



Zinc Oxide, ZnO , is manufactured by distilling zinc in a current of air or steam. It may be prepared by roasting zinc carbonate,



For use in pharmacy, it is obtained by mixing solutions of zinc sulphate and sodium carbonate when basic zinc carbonate is precipitated. This is collected, washed free from soluble materials, dried, and ignited. The product is very pure zinc oxide.

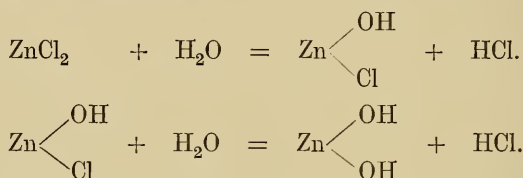
Zinc oxide is employed as a filling material for producing pink and grayish-white vulcanite. For the former, the white zinc oxide is mixed with vermilion (p. 97), and impregnated with the sulphur into the caoutchouc. For producing the grayish-white vulcanite, the vermilion is omitted. Zinc oxide is also used for making the basic zinc salts used as dental cements and adhesives. (see below).

Zinc Chloride, ZnCl_2 .—It has been mentioned that a solution of

¹ Galvanised iron is iron sheet which, after being cleansed, is coated with a layer of zinc by dipping it in the molten metal. This galvanised iron is particularly useful, since even if the zinc be scratched away from portions of the surface, the corrosion of the iron does not take place because the carbon dioxide necessary for the ordinary rusting of iron to take place appears to be retained by the zinc still remaining.

zinc chloride is also formed when zinc dissolves in hydrochloric acid and also when carbon dioxide is passed into an aqueous solution of calcium chloride containing zinc oxide in suspension. When anhydrous, zinc chloride is a soluble, deliquescent solid with a melting-point of 365°C . and a boiling-point of 730°C . The pure substance is used as a caustic for sensitive dentine and in cases of dentine erosion. In dilute aqueous solution it is used as an antiseptic and astringent in general septic conditions of the mouth.

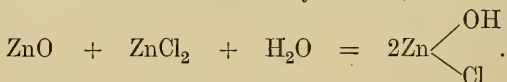
When a solution of zinc chloride is concentrated by evaporation, the zinc chloride undergoes hydrolysis with loss of hydrochloric acid, and mixtures of **zinc oxychloride** and hydroxide are formed,



This hydrolysis can be prevented by adding concentrated hydrochloric acid to the evaporating solution, and finally a crystalline hydrate, $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$, may be obtained.

Zinc chloride solution, generally containing some excess of hydrochloric acid and prepared when wanted by the action of zinc on hydrochloric acid ("spirit of salt"), is commonly used for cleaning the surface of metals before soldering.

When zinc oxide is mixed with an aqueous solution of zinc chloride, it sets to a hard mass of white zinc oxychloride,



This zinc oxychloride was formerly used as a dental cement for lining prepared cavities prior to insertion of the filling materials. The use of zinc oxychloride for this purpose has been to a great extent abandoned on account of the cement lacking in permanency. This is probably due to further hydrolysis taking place, forming zinc oxide, which is gradually washed away. Instead of zinc oxychloride, zinc oxyphosphate is now used to a considerable extent as a dental cement, and more particularly as an adhesive for lining the prepared cavity prior to filling.

Zinc Oxyphosphate, the composition of which has not yet been clearly determined, is formed by mixing zinc oxide with an aqueous solution of phosphoric acid (H_3PO_4). The mixture sets to a hard mass, which appears to last much longer in the mouth than zinc oxychloride, and is also less irritating. Zinc oxysulphate is also used to a small extent for the same purpose, but the use of basic zinc salts

as dental cements is now not nearly so extensive as formerly; they are being replaced by silicate cements, which seem to be much more suitable for the purpose (see p. 138).

Uses of Metallic Zinc : Alloys of Zinc.—As a metal zinc is used in Parke's process for the desilverising of lead (p. 72), and its alloys with copper, known as brasses, including German silver, have been described elsewhere (p. 82). One of the chief uses of zinc in the prosthetic laboratory is for the making of dies.

Notwithstanding the numerous alloys which have been introduced from time to time as a substitute for and an improvement upon zinc, this metal is by far the one most commonly used for the construction of dies for swaging metal dentures. Zinc melts at a comparatively low temperature, and the molten metal flows freely and yields a cast which is both tough and hard. The contraction which zinc undergoes on cooling is a disadvantage to its use for making dies, but the contraction is partly compensated for by the expansion which the plaster mould, from which the die is made, undergoes. For making a zinc die, the metal should be as pure as possible and, especially, free from lead. When cast at a temperature just above its melting-point, pure zinc yields a cast which does not appear to be highly crystalline. But when the metal is overheated and cast at a much higher temperature it becomes much more highly crystalline and brittle. Zinc is liable to become contaminated by its own oxide, and, to a small extent, by iron from the ladle in which it is fused. Oxidation may be minimised by covering the surface of the zinc with powdered charcoal, and the ladle used should be made of wrought-iron, the inside surface of which should be protected by a surface of whitening. Cast-iron seems to be somewhat easily attacked by molten zinc, and perforation of cast-iron ladles by molten zinc has been noticed.

Since a zinc die is frequently used with a lead counter-die, zinc often becomes contaminated with lead in the laboratory. It has been pointed out that zinc and lead, while partially miscible in the molten condition, are miscible only to a small extent in the solid state, the upper layer consisting of zinc containing about 1 per cent. of lead. If, therefore, the zinc has become contaminated with lead to a greater extent than 1 per cent., it is possible to separate it to this extent by liquation. The 1 per cent., or less, of lead must be got rid of by melting the zinc with a little sodium nitrate, whereby the lead is oxidised to litharge (PbO) and can be removed as a scum.

An alloy of Zinc and Tin composed of two parts by weight of zinc to one part by weight of tin has been recommended for making dies for the swaging of metal dentures. These two metals form an eutectic having a melting-point of 198°C . containing about 90 per cent. by weight of zinc, and an alloy of the composition used for making the zinc-tin die will therefore consist largely of the eutectic mixture with a smaller amount of zinc mixed with it. It has been found that this

alloy shrinks less than zinc alone, flows freely when molten in an open mould, and yields sharp castings. The melting-point of the alloy (about 330° C.) is about 90° C. lower than that of zinc and not very different from that of lead (327° C.), and for this reason it is of importance that the lead used in making a counter-die should be poured on to the zinc-tin die at as low a temperature as possible consistent with fluidity.

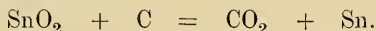
CHAPTER IX

TIN: TIN ALLOYS

TIN—Sn. (Atomic Weight=119); Valency, 2 and 4.

Occurrence.—The chief source of tin is the dioxide, SnO_2 , which occurs as the mineral **cassiterite**, or **tinstone**, in Cornwall. Tin from this source has been mined from very early times, and recently deposits of tin have been found in the East Indies and particularly in the island of Banca.

Extraction.—The metallurgy of tin is comparatively simple. The crude ore is roasted preliminarily in order to remove sulphur and arsenic in the form of their volatile oxides, and the roasted ore is mixed with anthracite and smelted in a reverberatory furnace, when the following reaction takes place,

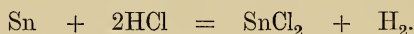


The molten metal is drawn off into moulds and is purified by remelting and running off from the less fusible impurities (liquation).

Properties and Uses of Tin.—Tin is a white, lustrous, highly crystalline metal which has a melting-point of $232^\circ \text{C}.$, and which exhibits, like iron, the property of **allotropy**. As in the case of iron, three forms of the pure metal are known, and therefore tin is described as being trimorphous. Grey or “amorphous” tin, having a specific gravity of 5.8, is the form stable below $18^\circ \text{C}.$; the tetragonal form, or ordinary white tin, is stable between $18^\circ \text{C}.$ and $161^\circ \text{C}.$, and has a specific gravity of 7.2; while the form stable between $161^\circ \text{C}.$ and the melting-point is rhombic, and has a specific gravity of 6.5. The tetragonal or ordinary crystalline form of tin is therefore metastable at all temperatures below $18^\circ \text{C}.$, but under ordinary conditions the change is very slow and may not set in for centuries. The change to the gray variety attains its maximum velocity at about $-50^\circ \text{C}.$, and cases are recorded in which articles made of tin, *e.g.* vessels, organ pipes, etc., have collapsed during severe winters owing to the change from the ordinary white form to the gray form. On account of the fact that the change from the ordinary white form to the gray takes place most rapidly when it is inoculated with the gray variety, as is the case in other examples of allotropy, it appeared that the change was spread by infection, and hence the change became known as **tin plague**. The change from the gray form to the ordinary white variety takes place rapidly when the former is simply covered with hot water. The change from white to gray tin is accompanied not only by disin-

tegration, but also by expansion, while the reverse change is accompanied by contraction in volume.

Tin is a malleable metal and can be rolled into thin sheets, known as **tin foil**. Tin is not acted upon by the atmosphere and is unaffected by hydrogen sulphide. It is dissolved by hydrochloric acid, when hydrogen is evolved and stannous chloride is formed,



Tin combines directly with chlorine, forming the liquid stannic chloride, SnCl_4 , and when acted upon by concentrated nitric acid it forms, not the nitrate, but an insoluble hydrated form of stannic oxide, SnO_2 . **Purple of Cassius**, which consists probably of stannic hydroxide coloured by colloidal gold, has been already described (p. 47).

On account of its resistance to corrosion under ordinary conditions, tin has been used for centuries for lining, or tinning, copper cooking-vessels which might otherwise be acted upon by weak acid liquids. The vessel is "tinned" by simply pouring molten tin into it and spreading the molten metal evenly over its inner surface. Tinplate, largely used for making the familiar so-called "tin" boxes, is thin clean iron sheet tinned by dipping into molten tin. The iron must be completely covered by the layer of tin otherwise rusting takes place very rapidly.

Pure tin is used as a filling material, being inserted and condensed in the same manner as non-cohesive gold, or, the foil may be rolled into cylinders and employed in the same way. Its softness renders it easy of adaptation to the cavity walls, and, since it is a relatively poor conductor of heat and electricity, it is compatible with the tooth substance. Since tin is not blackened by hydrogen sulphide it retains its colour in the mouth, but it does not resist attrition, and for this reason while the first half of the filling may be of tin the filling is usually completed with gold. Another method of using pure tin foil with non-cohesive gold has already been referred to. Tin foil and cylinders may be used to remove excess of mercury from amalgam fillings, and finely divided tin may be incorporated with an oxyphosphate cement in order to impart a better wearing surface to the latter.

Tin is used in the laboratory as a material for counter-dies for swaging dentures, replacing lead when a harder and more resistant counter-die is required. Since tin has such a small affinity for sulphur, and on account of its mechanical properties, stout tin foil is employed for polishing plates in the construction of vulcanite dentures. It not only imparts a smooth and polished surface to the vulcanite, but the quality of the latter is greatly improved, and rubber vulcanised in a tin-faced cast is rendered denser and tougher. The foil may be removed, if necessary, by dissolving it from the vulcanite by means of hydrochloric acid. Finely powdered tin, which can be easily

produced by vigorously shaking molten tin during solidification in a suitable box, is used for incorporating with rubber prepared for vulcanising in order to produce so-called "weighted rubber," occasionally used in the construction of lower dentures. It diminishes the amount of rubber used and also the porosity frequently noticed in a thick piece of vulcanite. Pure tin is also used in the construction of certain types of orthodontic appliances serving as a suitable solder for uniting the various cribs, springs, etc., to the basal wires of the apparatus.

Alloys of Tin.—The use of tin for hardening copper producing the varieties of bronze (p. 81), and the alloys of tin with silver which

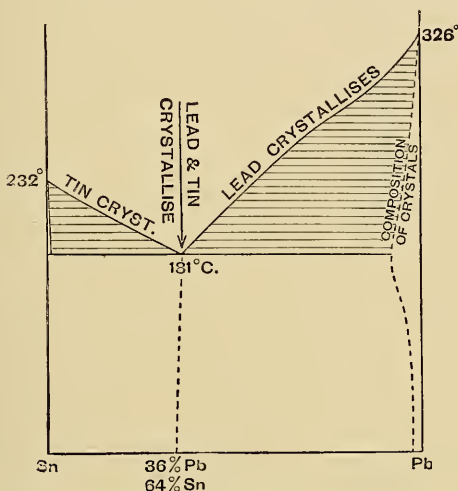


FIG. 17.—FREEZING-POINT DIAGRAM FOR TIN AND LEAD.

form the basis of most of the dental amalgams, have been described elsewhere (p. 94). The other important alloys of tin are those with lead as the other chief constituent; these tin-lead alloys find extensive use as soft solders. The melting-point curve of the tin-lead alloys shows that the two metals form an eutectic which melts and solidifies at 181° C. (Fig. 17). The eutectic mixture consists of 64 per cent. of tin (see also Fig. 9, page 38) and has the lowest melting-point of all tin-lead mixtures; lead dissolves about 16 per cent. of tin at the eutectic temperature, but tin separates in a nearly pure state from the liquid alloy. It is generally known as **fine solder**. Common solder is a mixture of equal parts of lead and tin which begins to solidify at about 220° C., and plumber's solder or **coarse solder** is a mixture of approximately equal parts of the two metals which begins to solidify at about 260° C., and it is remarkable and useful in having a large range of solidification, "pasty stage," of about 70° C. **Pewter**

is an alloy of tin and lead containing about 80 per cent. of the former metal. In contrast with silver, tin does not form a compound with mercury, and the solid tin amalgam is simply a solid solution of mercury in tin. The liquid tin amalgam, formerly used for coating mirrors, was prepared by the addition of mercury to a sheet of tinfoil pressed against the surface of the glass so as to squeeze out the excess of mercury.

Apart from their use as soft solders, the alloys of tin and lead form the basis of many fusible alloys in common use. These fusible alloys consist of metals which mix in all proportions in the liquid state, do not form intermetallic compounds, form solid solutions to a very limited extent, and give rise to eutectic alloys which melt at considerably lower temperatures than the pure metals. Of the more complicated fusible alloys, **Rose's alloy**, which consists of 1 part of tin, 1 part of lead, and 2 parts of bismuth, melts at 94°C. , and **Wood's alloy**, which consists of 1 part of tin, 2 parts of lead, 1 part of cadmium, and 4 parts of bismuth, melts at only 71°C. Such fusible alloys find important uses in the dental laboratory owing to their low melting-points. They serve as excellent dies for the lighter kinds of swaging, *e.g.* in the construction of crowns and bridges.

Type Metal, an alloy primarily used for the construction of type for printing purposes, possesses useful properties as a material for the construction of dies. It is sufficiently hard to resist defacement, and gives very sharp castings. The composition of type metal may vary considerably, but it usually contains 55 to 65 per cent. of lead, 8 to 30 per cent. of antimony, and 12 to 16 per cent. of tin. The antimony is added to promote expansion on cooling, and tin reduces the brittleness possessed by alloys of lead and antimony alone. Type metal generally fuses at about 260°C. , it is somewhat brittle, and, since the constituents tend to oxidise somewhat readily on melting in air, the alloy should be covered with a layer of charcoal to prevent oxidation during fusion.

Babbitt's Metal is another alloy sometimes used as a material for dental dies. The composition of the alloy recommended for dental purposes is 8 parts of tin, 2 parts of antimony, and 1 part of copper (Haskell). This alloy melts at a slightly lower temperature than lead, and it is suggested that a suitable material for the counter-die to be used with it, is an alloy consisting of 5 parts of lead and 1 part of tin, and further, to protect the surface of the die by a coating of whitening. Babbitt's metal is best prepared by fusing the copper and a portion of the tin, then adding the antimony and finally the rest of the tin. It is desirable that the surface of the molten alloy should be protected by a layer of charcoal so as to prevent the oxidation of the tin and the antimony during fusion.

Another tin alloy, important in dentistry, is **Britannia metal**. The composition of this alloy may vary considerably. It always con-

tains a large proportion of tin and certain smaller amounts of antimony and copper to increase the hardness and render it more tough and easily polished. Occasionally small amounts of zinc, bismuth, and lead are also added. The copper content is limited, otherwise the colour of the alloy is impaired and its melting-point becomes too high, while too great a quantity of antimony renders the alloy too brittle. The alloy is best made by adding the antimony and a portion of the tin to the molten copper, and finally adding the rest of the tin. During fusion, it is always necessary to protect the surface of the alloy from oxidation by means of a layer of charcoal. The fact that the specific gravity of the cast alloy is diminished by rolling is somewhat interesting. The alloy should be bluish-white in colour, hard, malleable and ductile, capable of being stamped or pressed into various shapes. It should also be perfectly fluid when molten, and yield good castings. Britannia metal is largely employed for making impression trays and many other articles used in dentistry. The following formulæ represent average kinds of Britannia metal :—

- (1) Tin 94 per cent., antimony 5 per cent., and copper 1 per cent.
- (2) Tin 90 per cent., antimony 6 per cent., copper 2 per cent., and bismuth 2 per cent.
- (3) Tin 80 per cent., antimony 10 per cent., copper 9 per cent., and lead 1 per cent.

No. (3) is specially recommended for castings. Another variety, known as Queen's metal, contains tin 89·5 per cent., antimony 7 per cent., and copper 3·5 per cent.

Tin Alloys Used for the Making of Cast Denture Plates.—On account of the fact that tin is particularly stable under oral conditions, and, since it forms a series of readily fusible alloys which are not irritating or toxic, cast base plates for dentures have been made for a considerable time from alloys which consist largely of tin. Besides tin, the usual metals for producing such alloys are bismuth, silver, gold, and, occasionally, antimony. Some of the alloys used, such as Weston's and Gartell's, are proprietary articles, but the compositions of the following have been published :—

- Kingley's alloy—tin 94 per cent., bismuth 6 per cent.
- Reese's alloy—tin 87 per cent., gold 4·4 per cent., silver 8·6 per cent.
- Bean's alloy—tin 95 per cent., silver 5 per cent.

These alloys are chiefly confined to the making of lower dentures, but they are not used so extensively as was formerly the case.

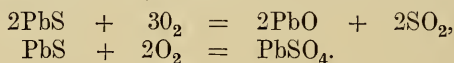
CHAPTER X

LEAD AND ITS ALLOYS

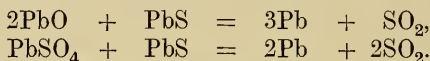
LEAD—Pb. (Atomic Weight=207.2); Valency=2 (chiefly).

Occurrence.—The chief ore of lead is the sulphide, PbS, or **galena**, which is found in large quantities frequently associated with zinc blende, ZnS, in Derbyshire and Shropshire, where the metal has been mined since the Roman occupation. Other less important ores of lead are the carbonate, PbCO₃, or **cerussite**, and the sulphate, PbSO₄, or **anglesite**.

Extraction of Lead.—The extraction of lead from galena depends on the partial oxidation of the sulphide to oxide and sulphate,



The mixture of oxide, sulphide, and sulphate are further heated in absence of air, when mutual reduction takes place with the separation of metallic lead and the evolution of sulphur dioxide,



Nowadays the smelting of lead is being carried out in small blast furnaces, but reverberatory furnaces are still being used (Fig. 18), in which the material to be heated is thrown on the bed of the furnace and heated by means of heat radiated from the roof. Fuel is burnt on the hearth by the side of the furnace bed.

In order to purify the lead, which is rendered hard by the presence in it of silver, arsenic, antimony, bismuth, copper, iron, and zinc, the crude metal is melted in an oxidising atmosphere. The arsenic, antimony, iron, and zinc are more easily oxidised than the lead, and the volatile oxides are got rid of while the non-volatile oxides separate as a scum. Copper and lead are only partially miscible in the liquid state, and the solid solution of copper and lead, containing 10 per cent. of the former metal, having a melting-point of about 957° C., is solid at a much higher temperature than the melting-point of lead, and therefore separates with the scum. The method of getting rid of the silver has already been described (p. 71), and the bismuth is eliminated at the same time.

Properties of Lead.—Lead is a bluish-white crystalline metal having a density of 11.34, a melting-point of 327.7° C., and a boiling-point of 1525° C. It is very soft and can be readily cut with shears.

On account of its being so plastic it can be squirted under pressure into the form of rods and pipes. It can be rolled into sheets and foil. Lead can be welded in the cold like gold, and, although lead becomes brittle on working, it returns to its original state at the ordinary temperature, whereas gold requires to be heated in order to anneal it.

On exposure to air the bright cut surface of lead rapidly becomes tarnished and dull, and when lead is melted for some time in air a layer of lead monoxide, PbO , or litharge, forms a scum on the surface of the molten metal. When litharge is further heated in air it is converted into red lead, a higher oxide which, when pure, has a composition represented by the formula Pb_3O_4 . Lead is not attacked by pure water in the absence of air, but water containing carbon dioxide dissolves lead, forming lead bicarbonate, $\text{Pb}(\text{HCO}_3)_2$. Hence

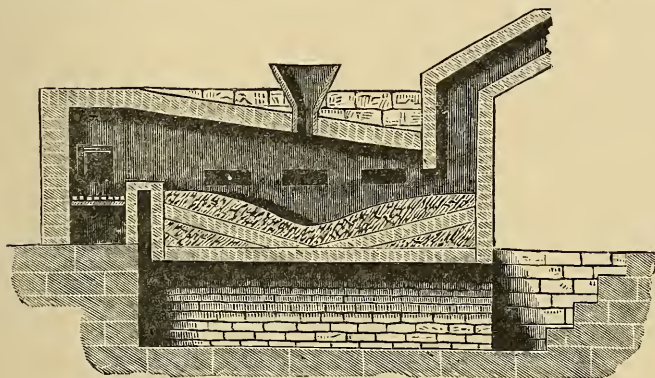


FIG 18.—REVERBERATORY FURNACE.

soft water conveyed through clean or fresh lead pipes may give rise to lead poisoning. Since the formation of lead bicarbonate is prevented by the presence of mineral salts, the same danger does not arise in the case of hard water.

Lead is readily soluble in nitric acid, oxides of nitrogen being evolved, and lead nitrate, $\text{Pb}(\text{NO}_3)_2$, being formed and precipitated if the solution of the acid is sufficiently concentrated. Lead is dissolved by concentrated sulphuric acid to a small extent with the production of lead sulphate,



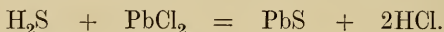
but the layer of lead sulphate apparently protects the lead from further attack. Similarly, concentrated hydrochloric acid attacks lead very slightly, hydrogen being evolved and lead chloride, PbCl_2 , formed, which being insoluble in the acid, prevents the further action on the metal.

Lead can be precipitated from solutions of its salts by metals which are more readily oxidisable. For example, the familiar *lead tree*

is obtained by allowing a zinc rod to stand in a solution of a lead salt,



The lead is deposited in the crystalline condition. Lead combines directly with chlorine, forming the white, highly crystalline lead chloride, and, with sulphur, forming the black lead sulphide, PbS . The formation of the black precipitate of lead sulphide by adding an aqueous solution of hydrogen sulphide to, or by passing the gas into, a solution of a lead salt, which may be either neutral or contain hydrochloric acid, constitutes a delicate test for the presence of lead,



The Uses of Lead in Dentistry.—The most important use of lead is as a counter-die in swaging denture plates. It is extremely valuable for this purpose since it has a low melting-point, it is soft and can be melted and worked up repeatedly without its properties being affected. When a counter-die of lead is used in swaging gold plate, it is highly important to keep the gold from actually coming into contact with the lead by protecting the latter with a covering of wash-leather or several layers of tissue paper. It has already been remarked that even small traces of lead render gold extremely brittle.

Alloys of lead and tin are used as soft solders, and are described elsewhere (p. 107); further, alloys of these two metals form the basis of many of the fusible alloys, such as Rose's alloy, which melts at 94°C ., and Wood's alloy, which melts at 71°C . The nature of these alloys and that of the form of Britannia metal, which contains lead and which is used for castings, are also described under "Alloys of Tin" (p. 107). Some specimens of aluminium bronze (p. 83) frequently contain small quantities of lead, as also do some kinds of brass and German silver. The lead is stated to be added to facilitate rolling.

The alloys of arsenic and lead do not appear to have been completely investigated. Lead and arsenic form an eutectic mixture melting at 292°C ., and which contains about 5 per cent. of arsenic. Arsenic renders lead hard and makes it brittle when present in excess. Arsenic is alloyed with lead for making lead shot, which is used in the dental laboratory for swaging crowns and base plates. It is conveniently used when Babbit's metal is employed for the die, as the latter is not damaged when the lower-melting molten lead shot is poured over it.

Pure lead foil finds important application in the assaying of gold and silver alloys (p. 52), where its use depends on its oxidation to the monoxide or litharge, PbO , which is absorbed by the cupel or flows away when present in such large quantities as are dealt with in the manufacturing processes (p. 66).

It need scarcely be pointed out that lead is a poisonous metal, and therefore is never used as a constituent of alloys which have to be employed in the mouth.

CHAPTER XI

IRON: ALLOYS OF IRON: PROPERTIES OF IRON

IRON—Fe. (Atomic Weight=55.84) ; Valency, 2 and 3.

INDUSTRIALLY, iron, in the form of its numerous alloys, generally referred to as varieties of iron, is the most important of the metals. The extraction of the metal from its useful ores is comparatively simple, and the modifications in properties which can be produced by combining iron with various metals and non-metals are so numerous that the study of the "ferrous" alloys occupies the premier place in metallurgy. Various varieties of steel are employed in dental practice, *e.g.* forceps, elevators, pliers, to mention only a few of the usual instruments, are made of steel, while orthodontic appliances, which have not only to be light, but have to be made of specially strong materials, are usually made of suitable varieties of the same alloy. The introduction of the incorrodible steels is of special importance in the dental laboratory. It is hardly necessary to call attention to the innumerable uses to which iron, or rather alloys of iron, are put in the laboratory. Not only is almost all the apparatus used for high temperature work constructed wholly or in part of this material, but so also is the apparatus which requires to be made of material capable of withstanding high pressure and strain without deformation.

Occurrence and Sources of Iron.—Iron, which is the fourth most abundant element in the earth's crust, has been found occasionally in considerable quantities in meteorites frequently associated with nickel and cobalt, and compounds of iron are very widely distributed in nature. Of the compounds of iron, only those which do not contain any appreciable quantities of such elements as sulphur, phosphorus, and arsenic are available as sources of the metal because if these elements are present in the finished metal the mechanical properties of the metal are seriously affected. The ores from which the metal is extracted contain either the oxides or carbonates of iron as their chief constituents.

Magnetic Oxide of Iron.—Ferroso-ferric oxide, Fe_3O_4 , is frequently found moderately pure. The famous Swedish iron is extracted from this ore, which is found in Sweden. It also occurs in large quantities in the region of Lake Superior. **Red Haematite**, the chief constituent of which is ferric oxide, Fe_2O_3 , occurs in a variety of forms which possess different physical characters. Specular iron ore and Kidney iron stone are two of the varieties of red haematite. It is found in

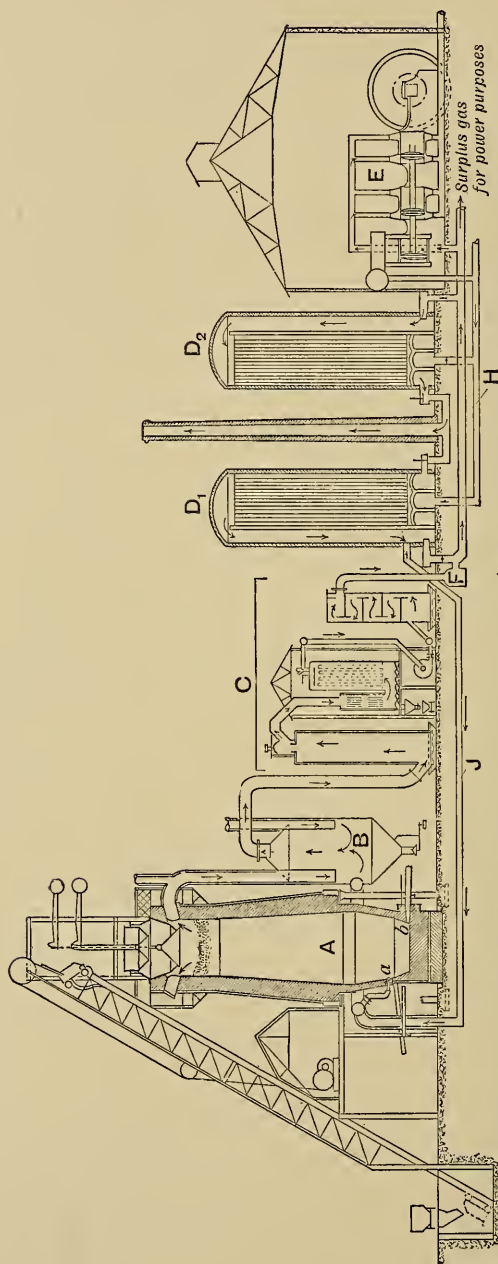


FIG. 19.—DIAGRAM OF BLAST-FURNACE, A, WITH MECHANICAL CHARGING GEAR, REGENERATIVE STOVES EMPLOYED FOR HEATING THE BLAST, ETC.

Cumberland, Spain, and in the neighbourhood of Lake Superior, and is especially valuable as being usually almost free from phosphorus. The different varieties of **Brown Haematite** also contain ferric oxide with varying amounts of water in a state of combination with the oxide. Such brown haematites are found in Spain, in the Forest of Dean, and in other parts of England. Many of the brown haematites contain appreciable quantities of phosphorus besides silica and calcium carbonate.

Spathic Iron Ore is the purest form of the naturally occurring ferrous carbonate, FeCO_3 . It is light brown in colour, and while containing manganese, is generally free from phosphorus. It is found in extensive deposits in many parts of Europe. **Clay Iron Stone**, formerly the most important iron ore in England, found in the neighbourhood of the large coal deposits, is a much less pure variety of ferrous carbonate, and contains appreciable quantities of phosphorus and manganese.

Sulphide ores of iron are found in considerable quantities, but these are sources of sulphur rather than of iron.

Production of Cast-Iron.¹—This is the initial stage in the manufacture of the various varieties of iron, and depends on the reduction (nowadays often without previous calcination) of its oxide contained in the ores, by means of carbon in the form of coke. The chief reactions which take place may be represented,



The operation is carried out in a blast furnace (Fig. 19), which may be as high as 80 feet, and, working continuously, capable of an output of as much as 1000 tons of cast-iron per week. The above equations only indicate the complete reactions; probably the reduction of the ferric oxide to the metal goes through the formation of ferrous oxide, FeO , as an intermediate stage. When the metal is produced in the upper part of the furnace, it absorbs carbon, which lowers its melting-point, melts and sinks down to the well of the furnace, whence it can be drawn off into suitable sand moulds where it solidifies in the form of **pig iron**. Such cast-iron is used in foundry practice on account of its low melting-point for making cheap castings, and it contains on the average about 4 per cent. of carbon and 2 per cent. of silicon, besides smaller quantities of manganese, phosphorus, and sulphur.

Wrought-Iron.—The production of wrought or malleable iron, the purest form of commercial iron, essentially consists in the freeing of cast-iron from the non-metallic impurities, which may be got rid of in

¹ As the working of iron is rarely, if ever, done in the dental laboratory, only the briefest outline of the metallurgy of the various forms of iron is given in the present work. Further information should be sought in the standard metallurgical works, e.g., Turner, *Metallurgy of Iron*, 1920 (Griffin).

various ways. Formerly this was accomplished by **puddling**, an operation which consisted in working the pasty mass of cast-iron at a red heat in contact with air. The carbon and phosphorus were burnt to their respective oxides, and these being volatile, were eliminated; and the silicon was oxidised to the dioxide, silica, SiO_2 . At the same time, some of the iron was oxidised to the magnetic oxide, Fe_3O_4 . The product was then subjected to hammering, by means of a steam hammer, to any desired extent, and an iron resulted which contained very little impurity besides traces of slag. The process has now been modified; the cast-iron is completely melted in the hearth of a reverberatory furnace in the presence of iron oxide (Fig. 20). Under these conditions the silicon and manganese are oxidised and form a slag, which also carries away most of the phos-

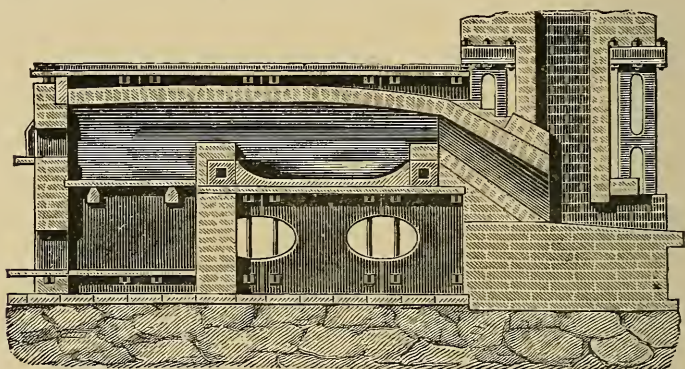


FIG 20.—FURNACE FOR MAKING MALLEABLE IRON.

phorus in an oxidised form. The carbon is oxidised to carbon monoxide by reduction of the iron oxide present, and the escape of the gas gives the appearance of boiling to the molten metal. As the various impurities are removed, the melting-point of the iron automatically rises, and the metal can be separated in the form of lumps. These lumps of solid metal are hammered and rolled at the welding temperature, when the characteristic fibrous structure of wrought-iron is developed.

Wrought-iron is characterised by its fibrous structure, by its remarkable toughness, and by its high tensile strength. Its chief use is in the production of certain high quality steels. For constructional work it has been largely replaced by the various grades of steel, but it is still employed for rivets and in blacksmith's work, and, generally, where welding has to be done.

Various qualities of **steel** may contain from 0.1 to 1.5 per cent. of carbon, and their manufacture from cast-iron consists not only in the reduction of the carbon content, but also in the almost complete removal of silicon and the elimination, as far as possible, of the

sulphur and phosphorus, both of which elements render the alloy brittle.

The **cementation** process, now being superseded, consists in heating wrought-iron bars with carbon for several days until the requisite quantity of the latter element is absorbed. The resulting product, known as **blister steel**, is converted by forging under a steam hammer into **shear steel**, used in making cutlery.

In the **Bessemer Process**, cast-iron was converted into steel by blowing air through the molten metal until almost all the carbon had been oxidised and got rid of, and the silicon oxidised to silica, which passed into the slag. To the product was added a certain amount of iron containing a known quantity of carbon and manganese (spiegeleisen) to produce the steel of desired quality. If the cast-iron contained little or no phosphorus, the "converter" (Fig. 21) had a silica lining. By lining the converter with lime and magnesia (Thomas and Gilchrist Process), cast-iron was freed from phosphorus because the phosphorus, when oxidised, is absorbed by the lining, forming basic slag, of great importance as an artificial manure in agriculture.

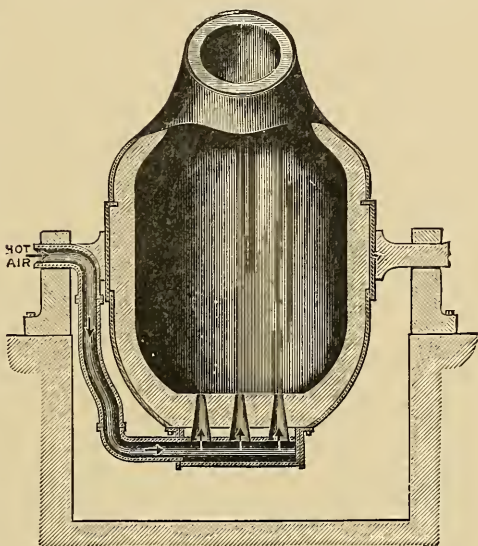


FIG. 21.—BESSEMER CONVERTER.

The Bessemer Process has been largely replaced by the **Siemens-Martin Process**, in which steel is produced by melting together in an open-hearth furnace (Fig. 22) cast-iron, wrought-iron, and iron oxide (often in the form of ore) in such quantities that the carbon is oxidised and eliminated to the required extent by the iron oxide. The process can be controlled with scientific accuracy, and the ingredients varied considerably. Phosphorus is eliminated by using a suitable lining to the furnace, and silicon is got rid of by being oxidised to silica, which is then absorbed by the lime, always added in considerable quantity, forming a slag of calcium silicate.

For the making of special steels, such elements as silicon, manganese, tungsten, and chromium are added during the process of manufacture as alloys of iron. Nickel is added as the free metal.

Properties of Iron and its Alloys.—Pure iron is a gray crystalline

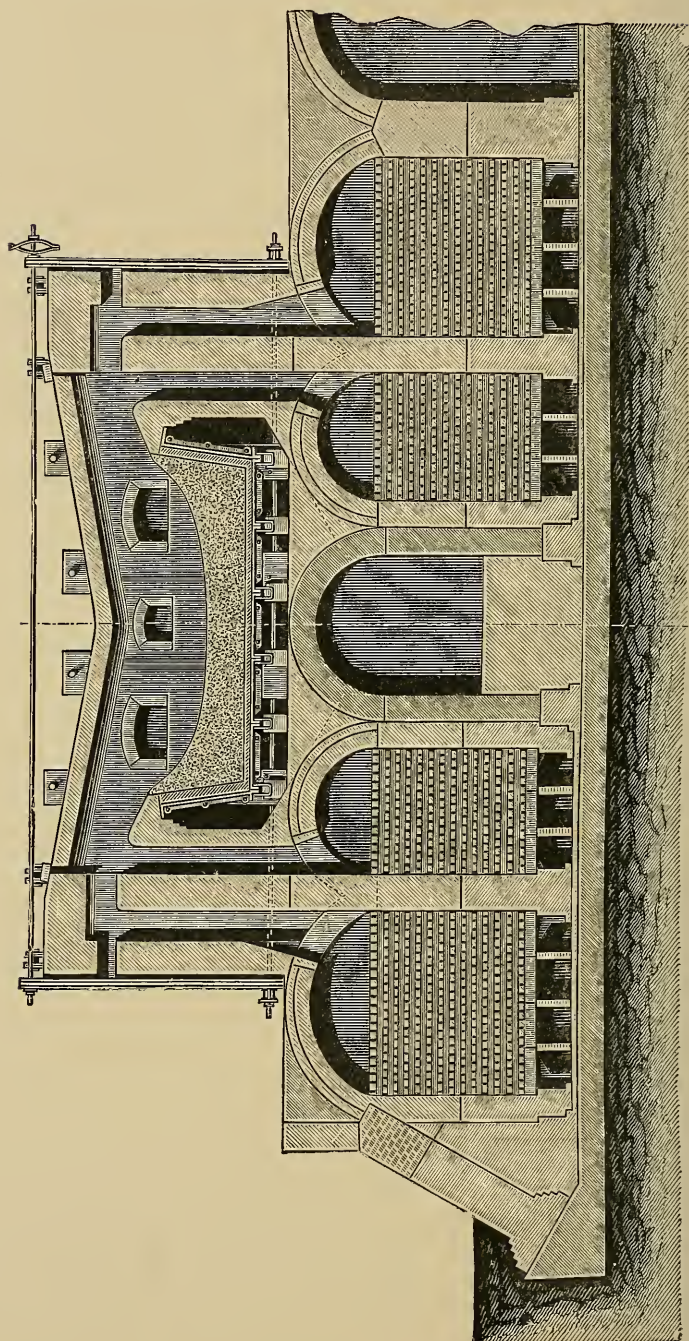


FIG. 22.—OPEN-HEARTH FURNACE.

metal, which melts at 1530°C. , and has a density of 7.8. A study of the cooling curve of molten iron has indicated that iron exists in allotropic forms, two of which, viz., the α -, which is stable up to about 766°C. , and is known as **ferrite**, and the γ -, which is stable from 896°C. to 1400°C. , are the most important. Ferrite, or α -iron, is the chief constituent of wrought iron, and which, on account of its magnetic properties, renders it invaluable for the construction of electro-magnets and transformers. γ -iron, on the other hand, is devoid of the magnetic properties of α -iron, and it is the chief constituent of many of the non-magnetic steels.

The melting-point of iron is lowered to a remarkable extent by the presence of carbon. The eutectic alloy of iron and carbon, containing 4.3 per cent. of the latter element, has a melting-point of 1150°C. , *i.e.* nearly 400°C. lower than the melting-point of pure iron, and this is the greatest extent to which the melting-point of iron can be reduced by carbon. Silicon also lowers the melting-point of iron, but not to anything like the extent that carbon does. Both carbon and silicon form compounds with iron (Fig. 23). The compound with carbon, known as **Cementite**, Fe_3C , gradually decomposes, when heated for some time at a temperature of 900°C. , into iron and carbon. Besides existing in the form of compounds, carbon and silicon can exist in iron, also in a state of solid solution, and as the free elements. Cementite is the hardest constituent of cast iron, and graphite the softest. Silicon seems to have a profound influence on the condition of carbon in cast iron. **White cast-iron** is the variety of lowest silicon content, and contains the carbon chiefly in the form of carbide, or cementite, while **gray cast-iron**, which contains much more silicon, has its carbon chiefly in the form of graphite.

The solubility of carbon in iron increases with increasing temperature. Thus, at about 700°C. , carbon is soluble in iron to the extent of 0.9 per cent., while, at 1150°C. carbon is soluble in γ -iron to the extent of 1.9 per cent. The solid solution containing 1.9 per cent. of carbon is therefore only stable at high temperatures, but it can be "fixed" at ordinary temperatures by quenching in water. This fixing of the solid solution is rendered all the more stable when small

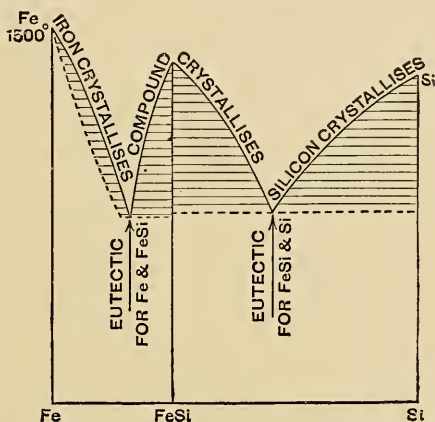


FIG. 23.—FREEZING-POINT DIAGRAM FOR IRON AND SILICON.

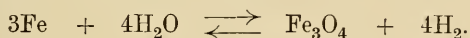
quantities of other elements, especially silicon and manganese, are also present. Such a **quenched steel** is known as **Austenite**, and contains the carbon probably in the form of the carbide. When the quenched steel is allowed to stand, the carbide tends to separate as such, and the steel then becomes very hard, forming the variety known as **Martensite**. Another variety of steel known under the name **Pearlite**, from its characteristic appearance, is produced from such a steel as Austenite. It is possible to supercool Austenite, which contains 0.9 per cent. of carbon in solid solution in γ -iron, to a temperature of about 700° C. Below this temperature α -iron is the stable form, and therefore the γ -variety passes into the α -form, a change which is accompanied by evolution of heat. At the same time, the excess of carbon separates as carbide. The evolution of heat causes the alloy to glow again, when the ordinary glowing of the hot mass has ceased. This phenomenon, known as **recalcescence**, accompanies the formation of pearlite.

The production of special steels, containing such elements as manganese and nickel, depends on the fact that these metals form solid solutions with γ -iron in all proportions, but not with α - (or magnetic) iron. Further, by means of these solid solutions, the temperature of conversion of γ -iron into the α -variety can be lowered to almost any desired extent, and consequently the alloys produced not only contain the requisite amount of carbon, on which their hardness primarily depends, but also are permanently non-magnetic. **Manganese steel** is particularly used on account of its non-magnetic properties. The manganese steels are specially tough, and possess remarkably high tensile strength. They are also largely employed where resistance to excessive wearing is necessary. The solid solutions of nickel and iron are only stable at high temperatures and at lower temperatures a compound of iron and nickel, FeNi_2 , may separate together with α -iron, with which nickel does not form solid solutions. The **nickel steels** are especially remarkable in having practically no co-efficient of expansion over a considerable range of temperature. These alloys, under the name of **Invar**, are therefore used in the construction of instruments of precision, such as standards of length, surveying instruments, pendulums, and generally for purposes where constancy of length is essential. Stainless steel used for cutlery is a **chromium-iron** alloy of low carbon content.

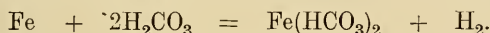
Steels used for making high-speed tools are complex iron alloys, containing varying amounts of such metals as tungsten, chromium, and vanadium, besides small quantities of the non-metallic elements, carbon and silicon. These alloys retain their hardness, and, at the same time, preserve their cutting edge at temperatures where simple steels become soft.

Oxidation and General Chemical Properties of Iron.—Dry air or oxygen has no visible action on iron at ordinary temperatures; but at a temperature of a little over 200° C. oxidation begins, the iron

first assuming a yellow tint, and finally a blue colour, as the temperature rises. These "tempering" colours, the occurrence of which are made use of in tempering steel commercially, are due to the formation of thin layers of oxide. When iron burns in oxygen, the black magnetic oxide, Fe_3O_4 , is formed, and the same oxide is produced by the action of steam on iron at a red heat. In the latter case, the action is reversible, and is represented,



The phenomenon of the **rusting of iron** has been the subject of a large number of investigations, since a knowledge of the subject is of so great industrial importance. Iron rust which has been formed for some considerable time, and may be regarded as being completely oxidised, has a composition approximately represented by the formula, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and is therefore hydrated ferric oxide. When freshly formed, however, iron rust contains also ferrous oxide, FeO , in a hydrated form, and also ferrous carbonate, FeCO_3 . The precise mechanism of the process of rusting has, even yet, not been fully elucidated. Undoubtedly, liquid water and air, or oxygen, are essential for rusting to take place, and since ferrous carbonate has always been found to be present in newly formed rust, it has been suggested that iron dissolves in carbonic acid, the solution of carbon dioxide in water, producing ferrous bicarbonate and hydrogen,



The ferrous bicarbonate in solution is then oxidised by oxygen dissolved in water to ferric hydroxide—ferric carbonate does not exist—carbon dioxide is liberated, and so is available for further rusting to take place,



The ferric hydroxide can lose a portion of its water, and so produce the fully oxidised rust. It has long been known that the presence of alkalis which are capable of combining with carbon dioxide prevent rusting to a considerable extent, and this theory indicates, as was proved by Moody¹ and Friend,² that iron to undergo rusting must first be in solution, and that carbon dioxide is necessary. On the other hand, Whitney³ and Walker⁴ maintain that the presence of carbon dioxide is unnecessary, believing that iron is capable of dissolving to a small extent, but progressively, in water with actual liberation of a chemically equivalent amount of hydrogen and the formation of ferrous hydroxide. The small amount of ferrous hydroxide in solu-

¹ *Trans. Chem. Soc.*, 1906, **89**, 720; *Proc. Chem. Soc.*, 1907, **23**, 84.

² *Jour. Iron and Steel Inst.*, 1908, ii, 16; *Proc. Chem. Soc.*, 1910, **26**, 179.

³ *Jour. Amer. Chem. Soc.*, 1903, **25**, 394.

⁴ *Ibid.*, 1907, **29**, 151.

tion during any short interval of time is oxidised to ferric hydroxide, and this, being less soluble, is deposited. Still another theory has recently been put forward, and experimental evidence supporting it produced by Friend.¹ According to this theory, although iron goes into solution in water, with extreme slowness, to form colloidal ferrous hydroxide, this is then rapidly oxidised by dissolved oxygen to a colloidal higher hydroxide, which now acts catalytically by oxidising metallic iron rapidly, being itself reduced again to ferrous hydroxide, which can then be reoxidised by dissolved oxygen, and the process repeated.

It is natural that most of the work on the investigation of the rusting of iron has been carried out on good specimens of commercial iron, usually wrought iron and steel, but Lambert, in a series of very careful investigations, has conclusively proved² that chemically pure iron remains unchanged when exposed to purified air and pure water for several months. When the iron contains even a minute trace of impurity, rusting takes place under these conditions. This interesting behaviour of pure iron substantiates Lambert's theory, that pure iron is chemically inactive, or "passive," to reagents, and does not dissolve in water even to a small extent, and that substances, *e.g.* alkalies, alkali carbonates, chromates, etc., which have been shown to prevent the rusting of commercial iron, also render iron passive. In this connexion it is interesting to note that such elements as phosphorus, nickel, chromium, and silicon, which may be present in iron, form alloys highly resistant to corrosion, and that chromium is the important element alloyed with iron in the modern stainless steels.

Iron dissolves readily in dilute mineral acids, producing in the case of hydrochloric and sulphuric acids ferrous salts and hydrogen,



When carbon is present in commercial iron in the form of carbide, Fe_3C , hydrocarbons are evolved in addition to hydrogen, whereas when carbon is present, as free carbon or graphite, the latter remains undissolved.

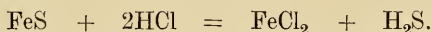
In concentrated nitric acid, iron does not dissolve, but is rendered "passive," and this passive iron so produced does not dissolve in weaker acid solutions. Possibly the iron becomes coated with a highly resistant film of oxide which prevents the metal being attacked.

Iron unites directly with the halogens, and with phosphorus it forms directly a compound having the formula Fe_3P . Similarly with silicon, it forms compounds, FeSi and Fe_2Si . The compounds of iron with silicon and with carbon have already been mentioned in connexion with the iron alloys.

¹ *Trans. Chem. Soc.*, 1921, **119**. 932.

² *Ibid.*, 1910, **97**. 2426, and later papers in the same Journal.

When heated together, iron (in the form of filings) and sulphur combine together with considerable evolution of heat to form ferrous sulphide, FeS , a black compound which melts at about 1200°C ., and which can be cast into rods. In this form it is used as the source of hydrogen sulphide, H_2S , in the chemical laboratory, the gas being produced by the action of dilute hydrochloric acid in the familiar Kipp's apparatus,



Ferrous sulphide, dissolved in an excess of sulphur, forms the so-called "**Spence's Metal**," which finds application in the dental laboratory as a finishing die in metal work. It is also useful for casting impressions for fused porcelain inlays where the matrix has to be swaged to the cast. It is very brittle, and melts at a low temperature, and does not contract on setting. When melted it flows easily, and when solid is sufficiently strong. It is, however, very brittle, and since sulphur boils at 444.5°C ., it cannot be heated very strongly, otherwise loss of that element will take place, and the strength of the material for die purposes seriously diminished. The Spence's Metal usually employed for dies is made by heating together iron filings and an excess of sulphur. Occasionally it may contain other sulphides, such as those of lead, antimony, and zinc, to confer special properties.

CHAPTER XII

NICKEL AND ITS ALLOYS

NICKEL—Ni. (Atomic Weight=58.68); Valency, 2.

Occurrence.—Nickel in small quantities is fairly widely distributed in nature, but the only really abundant ores are **garnierite**, a hydrated silicate containing 7 to 10 per cent. of the metal, found in New Caledonia, and the nickeliferous pyrites of indeterminate composition found in Ontario. Other metals, chiefly iron, cobalt, and copper, combined with arsenic, antimony, and sulphur almost always occur with nickel in ores which are found in many countries. Nickel is an essential constituent of meteoric iron, and meteorites have been found containing more nickel than iron.

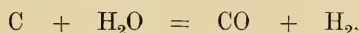
Extraction of Pure Nickel.—The metallurgy of nickel is complicated by the fact that its extraction involves a separation from copper and iron in addition to the final isolation of the metal.

The sulphide ores are first roasted to get rid of excess of sulphur, and then melted in small blast furnaces. As in the case of the extraction of copper, the ferrous sulphide is converted into ferrous oxide, which combines with silica present to form a slag of ferrous silicate (FeSiO_3), and the mixed sulphides of nickel and copper, which still contain a large percentage of iron, separate below. The mixed sulphides are then oxidised in the presence of sand, in a Bessemer converter, provided with a silicate lining, in order to get rid of the remaining iron, which is converted into ferrous silicate. The ferrous silicate takes up a small amount of nickel, and is worked up with fresh ore.

In working up the silicate ores, these are first converted into sulphides by smelting with calcium sulphate and charcoal (or calcium sulphide itself may be used). Calcium silicate is produced as a slag, and the resulting sulphides are worked up in the manner described above.

The fact that nickel combines with carbon monoxide at temperatures below 100°C. to form nickel carbonyl (NiC_4O_4), a poisonous liquid which boils at 43°C. , and which is decomposed at $180\text{--}200^\circ \text{C.}$, depositing nickel and liberating carbon monoxide, is made use of in the **Mond** process for separating pure nickel from its ores. In this process, the mixed sulphides of nickel and copper, containing a small amount of iron, obtained in the manner already described, are roasted so as to get rid of all the sulphur as sulphur dioxide, and to convert the metals into their oxides. The mixed oxides are then extracted

with dilute sulphuric acid, by which the copper and iron oxides are dissolved preferentially to the nickel oxide, NiO . The undissolved portion is now much richer in nickel and less rich in copper and iron than before extraction. The oxides are heated in a current of **water gas**—a mixture of hydrogen and carbon monoxide, produced by passing steam over red-hot coke,



at a temperature of about 300°C . Under these conditions, the nickel and copper oxides are reduced to the respective metals, whilst the iron oxide is unaffected. The reduction is chiefly effected by the hydrogen, and the residual gas, now richer in carbon monoxide, can be used for the formation of nickel carbonyl, after first being passed over hot charcoal in order to reduce any carbon dioxide to the lower oxide.



The mixture of nickel and copper, which also contains iron oxide, is now heated at a temperature of 50 – 100°C . in a current of carbon monoxide (80 per cent. obtained from the previous part of the process) and the volatile gas, containing some 2 per cent. of nickel carbonyl, is then decomposed at about 180°C . in a decomposing tower, containing small pellets of pure nickel, on which the nickel now produced is deposited. The remaining metal mixture requires further activation by water gas, and the gas from the decomposing tower is used over again for producing nickel carbonyl.

Nickel, as produced by the Mond process, is of a very high degree of purity (99.8 per cent.), and contains merely traces of iron, carbon, and sulphur as the chief impurities. As extracted by the older metallurgical processes, it was necessary to refine nickel by electrolysis, using a solution of nickel ammonium sulphate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, as the electrolyte, in a somewhat similar manner to that employed in the process of nickel-plating described below.

Properties of Nickel.—Nickel is very similar to iron in many of its properties. It is steel-gray in colour, and takes a very high polish. Like iron it is magnetic, but its magnetic properties disappear when the metal is heated. Its melting point (1452°C .) is somewhat lower than that of iron, and its density (8.8) is higher. The tensile strength of nickel is greater than that of iron.

Nickel shows much less tendency to combine with oxygen than iron does, and articles made of nickel or nickel-plated articles do not rust in air. It dissolves very slowly in dilute hydrochloric and sulphuric acids, but more readily in nitric acid. It is not attacked by alkalis, and hardly appreciably by hydrogen sulphide. Its resistance to oxidation and ordinary chemical reagents has led to the use of nickel in the making of spatulas, crucibles, tongs, etc., for laboratory

work. For the same reason, articles made of steel (instruments, etc.) are frequently covered with nickel, generally over copper, so as to prevent their rusting.

Since nickel is so hard, it is almost impossible to burnish it after it has once been deposited, and therefore, previous to **nickel-plating**, the surface to be plated must be burnished until perfectly smooth and bright, otherwise the deposited metal will reproduce, in an exaggerated form, all the irregularities of the surface. After being burnished, the surface to be plated is cleaned in the alkaline bath, and first covered with a very thin deposit of copper by electrolysis (copper-plating, see p. 80). The article is then made the cathode, and a piece of pure nickel the anode, in an electrolyte consisting of nickel ammonium sulphate (25 grams), ammonium sulphate (12 grams), dissolved in water, and rendered strongly alkaline with ammonia, the whole being made up to 500 c.c. with distilled water. A bath nearly boiling, but not so hot as to expel the ammonia, furnishes as a rule a better deposit than one at the ordinary temperature. For the first few minutes the current passed through should be about four or five times as strong as the normal strength, which secures the rapid deposition of a very thin but uniform deposit of nickel, on which the main deposit can be more slowly deposited without any local chemical interference from the original metal. The strength of the current used is similar to that employed in copper-plating.

Alloys of Nickel.—The alloys of nickel are attaining considerable industrial importance. Those with iron, the nickel steels, are especially remarkable for their toughness and constant elasticity over a range of temperatures, and have been employed in the making of armour-plate and for watch springs. While nickel only forms a complete series of solid solutions with iron at high temperatures, it forms complete series of solid solutions with cobalt and with copper, which are stable at all temperatures. The copper alloys with nickel, which, of course, all melt at temperatures higher than the melting point of copper, are probably the most important from the dental point of view, and of these, German silver, which contains zinc in addition to copper and nickel, has already been described (p. 82). Nickel coins usually contain about 25 per cent. of copper, and alloys containing higher proportions of copper are used in electrical work, on account of their high resistance and low temperature co-efficient. **Constantan**, which is an alloy of nickel and copper, containing about 60 per cent. of the latter metal, is an alloy used for such purposes.

Nickel alloys are now being used as a substitute for platinum for making the pins for artificial teeth.

CHAPTER XIII

CADMIUM, ANTIMONY, AND BISMUTH

CADMIUM

Cd. (Atomic Weight=112.4); Valency, 2.

Occurrence.—Cadmium is a comparatively rare metal. The chief source of the metal is from zinc ores, where it occurs in varying amounts from 1 to 5 per cent. Cadmium sulphide, CdS , occurs in the rare mineral, greenockite, found in the Glasgow and Greenock tunnel near Bishopton, in Renfrewshire.

Extraction of Cadmium.—In the smelting of zinc ores (especially blende), which contain cadmium, the cadmium oxide, CdO , is more easily reduced by the carbon than zinc oxide, and cadmium also has a lower boiling-point than zinc. Consequently, the vapours which come over first in the distillation contain most of the cadmium. These vapours burn with a brown flame due to the cadmium. The cadmium can be extracted by re-distilling with coal the first portion of the dust which collects in the condensers used in the distillation of zinc.

Other methods of obtaining cadmium depend on the precipitation of cadmium by means of zinc from solutions of zinc salts containing cadmium, and subsequent purification of the precipitated metal after casting by electrolysis. The cadmium may be conveniently deposited on a platinum cathode, from which it can be readily obtained by distillation.

Properties of Cadmium.—Cadmium is a highly lustrous, bluish-white metal. It melts at 321.7°C . and boils at 778°C . At ordinary temperatures it is malleable and ductile, but becomes brittle on heating to 80°C ., and at that temperature it can be powdered in a mortar (compare zinc).

When heated in air, cadmium burns, producing white fumes of cadmium oxide. Cadmium dissolves like zinc, but somewhat less readily, in hydrochloric and sulphuric acids with evolution of hydrogen and the formation of cadmium chloride, CdCl_2 , and cadmium sulphate, CdSO_4 , respectively.

The chief uses of cadmium are in the preparation of the low fusing alloys containing lead, tin, bismuth, and cadmium. The most important one of these is Wood's alloy, already referred to (pp. 103, 112), which melts at 71°C ., and is used for the making of dies used against a lead counter-die in the swaging of gold denture plates.

The use of cadmium as a constituent of the alloys used for the making of dental amalgams has now been abandoned. Although

cadmium hastens the setting of an amalgam, the formation of yellow cadmium sulphide by the action of hydrogen sulphide makes it an undesirable constituent of such alloys.

ANTIMONY

Sb. (Atomic Weight=120·2); Valency=3 and 5.

Occurrence.—The most important antimony ore is the sulphide **stibnite**, Sb_2S_3 , which is a gray-black mineral possessing a highly metallic lustre. Stibnite is remarkable for the highly crystalline nature of many of its specimens. Antimony also occurs in many mineral sulphides, in which it partially replaces sulphur, *e.g.*, the mineral NiSbS , which is isomorphous with iron pyrites, FeS_2 . Antimony also occurs as sulphide in many copper and silver ores, *e.g.* $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ and $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$.

Extraction of the Metal.—The method of extraction of antimony from the sulphide is comparatively simple, and consists in reducing the sulphide with metallic iron,



The iron sulphide forms a slag and floats on the molten metal. The crude metal, which may contain arsenic, sulphur, and iron as the chief impurities, is purified by heating with iron sulphide and such a salt as potassium carbonate or sodium sulphate. Under these circumstances the arsenic and sulphur pass into the slag as a soluble thioarsenite, and the iron also combines with the sulphur, forming ferrous sulphide, which floats with the slag on the surface of the molten metal. The purification may have to be repeated several times.

Properties of Antimony.—Antimony is a lustrous silver-white metal which shows a characteristic laminated crystalline fracture. Crystals of antimony obtained by the rapid cooling of the molten metal are almost cube-like in appearance. Antimony has a density of 6·62, and a melting-point and boiling-point of 630°C . and 1440°C . respectively. It is a particularly brittle metal, and remarkable for the large number of inter-metallic compounds it is capable of forming. Owing to the fact that molten antimony expands on crystallisation, it is valuable in making casts.

Antimony is stable in air, but when heated in the presence of air or oxygen it burns to the oxide, Sb_2O_3 , which is also formed when antimony is oxidised with nitric acid. It combines directly with chlorine, forming the trichloride, SbCl_3 , and also with sulphur and phosphorus when heated. The metal is not affected by dilute hydrochloric or sulphuric acids. It dissolves in hot concentrated hydrochloric acid in the presence of oxygen, giving the trichloride, SbCl_3 , and it also dissolves in hot concentrated sulphuric acid, yielding the sulphate, $\text{Sb}_2(\text{SO}_4)_3$. The first product formed on heating the metal in air is antimonious oxide, Sb_2O_3 , which is capable of dissolving both

in acids and alkalis, being therefore described as an amphoteric oxide.¹ With acids, *e.g.* hydrochloric and sulphuric acids, salts of antimony, SbCl_3 and $\text{Sb}_2(\text{SO}_4)_3$, are formed, and with alkalis salts of antimonious acid, H_3SbO_3 , are produced.

Uses of Antimony in Dentistry.—The chief use of antimony in dentistry is as a constituent of the alloys used for dies and counter-dies. Many of these have been already referred to (p. 108). Most of these alloys contain tin, and the chief of them are type metal and Babbitt's metal. Britannia and Queen's metal, used for castings, also contain antimony. Antimony present in alloys has a hardening effect, and, as one would expect, causes the alloy to expand slightly on solidification.

Antimony is a poisonous metal, and therefore is never a constituent of alloys used in the mouth.

BISMUTH

Bi. (Atomic Weight = 208.0); Valency = 3 (chiefly).

Purification of Bismuth.—The chief source of bismuth is the native metal, which is generally contaminated with antimony and arsenic,



FIG. 24.—METALLIC BISMUTH.

both of which elements are isomorphous with it, and are placed in the same group of the Periodic Classification of the Elements.

The naturally occurring bismuth is first melted and run off from

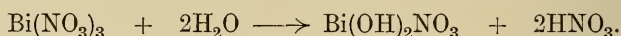
¹ Antimonious oxide, Sb_4O_6 , is used for the preparation of *tartar emetic*, potassium antimonyl tartrate. This substance is formed when antimonious oxide is boiled with a suspension of potassium hydrogen tartrate, $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$, in water. On filtering the hot solution, potassium antimonyl tartrate, $\text{K.SbO.}(\text{C}_4\text{H}_4\text{O}_6)$, crystallises out in characteristic colourless crystals,



the non-metallic substances contaminating it. The metal so obtained is then melted with sodium or potassium nitrate, which oxidises the arsenic and antimony present to sodium (or potassium), arsenate, and metantimonate, Na_3AsO_4 and NaSbO_3 respectively. These salts are highly soluble in water, and can be got rid of quite easily.

Properties of Bismuth.—Bismuth is a lustrous grayish-white metal, having a density of 9.8. The crystals of bismuth are very beautiful and highly characteristic. They consist of large skeletal-like cubes, which possess a reddish tinge, possibly due to slight tarnishing (Fig. 24). The melting-point of bismuth is only 271°C. , while its boiling-point is 1420°C.

When heated in air bismuth burns to the trioxide, Bi_2O_3 . It combines directly with chlorine, forming the liquid trichloride, BiCl_3 . Bismuth is scarcely affected by hydrochloric acid, but it dissolves in concentrated nitric acid, forming bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$. Bismuth nitrate is a crystalline soluble deliquescent salt, which is hydrolysed by water and converted into the sparingly soluble basic nitrate, $\text{Bi}(\text{OH})_2\cdot\text{NO}_3$.



Bismuth basic nitrate is the "Bismuth Subnitrates" of the pharmacopœia, and is used chiefly in the treatment of gastric catarrh and ulcer, and, on account of its astringent and protective action on the intestine, has also been used in the treatment of diarrhœa.

Uses of Bismuth in Dentistry.—Bismuth is, like antimony, too brittle for it to be used except when alloyed with other metals. Like antimony, it expands on solidification, and because of this, and of its low melting-point, it is found as a constituent of the low fusing alloys such as Rose's alloy and Wood's alloy, both of which have already been described (p. 108). These alloys are used for making dies to be employed with a lead counter-die in the swaging of gold denture plates.¹ Some specimens of Britannia metal contain bismuth (p. 108), and here the metal is used to give rise with the antimony, also present, to the necessary expansion on solidification.

¹ Another use for the low fusing alloys containing bismuth is in fire protection apparatus for closing automatic sprinklers.

PART II

MISCELLANEOUS MATERIALS USED IN DENTISTRY

CHAPTER XIV

PORCELAIN, PLASTER OF PARIS, AND DENTAL CEMENTS

PORCELAIN

OF the substances containing aluminium used in prosthetic dentistry, **Porcelain** is of very great importance. For nearly a century porcelain has entirely replaced all other materials for the manufacture of artificial teeth. It is also used for the construction of continuous gum dentures, for crown and bridge work, and as a filling material in the form of porcelain inlays. Different grades of porcelain are required for these various purposes, and the necessary properties are secured by alteration in the character and amounts of the ingredients used in their manufacture.

In its broadest sense, porcelain is a fine kind of earthenware having a translucent body and a transparent glaze. Dental porcelain is described as being a hard porcelain, and the chief materials used for making it are felspar, white china clay, and silica. Starch is also added in small quantity, since it makes the material, after firing, sufficiently hard to be trimmed to the requisite size. As a material for the making of artificial teeth, etc., porcelain is almost an ideal substance. It is sufficiently strong for mastication purposes; its conductivity for heat allows soldering to be carried out without fracture; it is sufficiently dense to allow of its ground surface being repolished, and its colour can be easily varied so as to approximate to that of natural teeth.

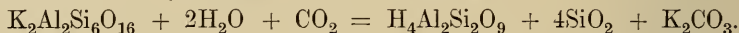
Like natural teeth, artificial substitutes are composed of two distinct portions, viz., the "body" or base, which corresponds to the dentine, and the enamel. For the body, besides the materials mentioned above, a little titanium oxide, TiO_2 , is added so as to impart the cream-yellow tinge of the dentine. For producing the enamel a so-called "frit" is used, which consists of similar ingredients to those used in producing the body, together with inorganic colouring materials, but the amounts of the various ingredients are such as to produce a lower fusing material than that of the body.

Silica, silicon dioxide, SiO_2 , occurs naturally in large quantities, both in the transparent hexagonal crystalline form as **quartz** or **rock crystal**, and also in the amorphous condition as **jasper**, **opal**, and as

the different varieties of **chalcedony**, such as **agate**, **carnelian**, and **chrysoprase**. White sand is almost pure silica, and has probably been formed by the "weathering" of silicious rock. Yellow and brown sand is silica coloured chiefly by iron oxide. Silica melts in the oxyhydrogen blowpipe to a colourless glass, its actual melting-point being somewhat indefinite. It is completely insoluble in water and all acids except hydrofluoric acid. It should be regarded as an acidic oxide, since it combines at high temperatures with such oxides as calcium oxide (CaO), lead oxide (PbO) to form silicates or salts of silicic acid; it is also capable of replacing carbon dioxide in sodium carbonate with the production of sodium silicate (Na_2SiO_3), a solution of which in water forms the so-called "water glass." The finest varieties of rock crystal are used for making porcelain teeth. The hard masses are split into smaller pieces by heating to redness and then dropping into cold water; these are again reduced by grinding with pestle and mortar, and finally levigated to an impalpable powder. Silica is used for the purpose of imparting stability to porcelain, and to assist in retaining its shape during firing.

Of the many varieties of **felspar**, **potash felspar** is the one used in the manufacture of porcelain. This felspar may be regarded as a double silicate of potassium and aluminium of the composition $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. It forms the matrix of granite rocks, which, when subjected to "weathering," disintegrate and leave behind clay mixed with the more resistant varieties of mica (complex silicates of aluminium and the alkali metals together, in some cases, with iron and magnesium), quartz and other minerals present in the rock.

Clay is a hydrated aluminium silicate. It is a colloidal substance, and has the characteristic property of being plastic when wet and of baking to a hard mass when heated strongly. It has a much higher fusing-point than felspar, and is the highest fusing of the chief substances used in the making of porcelain. The residual clay formed by the weathering of granitic rocks containing little iron, after being subjected to an elaborate process of washing and settling,¹ forms **white china clay**, whose composition may be approximately represented by the formula, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and the action, bringing about its formation from felspar, may be represented,



Under the conditions of manufacture of porcelain, the white china clay or kaolin remains infusible, but unites with the selected and finely ground felspar, which has a much lower fusing-point.

The following represents the composition of a typical mixture for the preparation of the "body" porcelain of artificial teeth:

¹ An electrical process for the purification of china clay is employed in modern practice. The use of this process depends on the colloidal nature of the clay, and is extremely efficient.

Kaolin 1 oz., Silica 3 oz., Felspar 18 oz., Titanium oxide 65 gr., and Starch 10 gr. to each ounce. The starch and titanium oxide are first ground together; the kaolin and the silica are then added and ground. This mixture is then sifted through a fine sieve, and lastly the felspar is added, and the whole thoroughly ground, and the mixture finally sifted for use.

From an æsthetic point of view it is important that the artificial tooth should resemble the natural variety as closely as possible, and therefore the pigmenting of porcelain teeth forms an important part of their manufacture. The enamel of the natural tooth is represented by the glaze or enamel of the porcelain, which can be suitably tinted. The frits for the production of the glaze contain the pigmenting substances mixed with felspar, and such a flux, as a mixture of silica, sodium borate, and potassium carbonate, all ground very finely, fused into a glass and finally reground for use. The following pigmenting substances find applications:—

Titanium Oxide, TiO_2 , for producing the yellow colour of the enamel in addition to the cream-yellow colour of the dentine.

Cobalt Oxide, Co_2O_3 , for producing blue tints of enamel.

Ferric Oxide, Fe_2O_3 , is used for producing gray tints.

Platinum sponge is also used for producing gray tints.

Gold is used for producing reddish-brown tints.

“Purple of Cassius” (see p. 47), which may be regarded as a precipitate of finely divided or colloidal gold on hydrated stannic oxide, is used for producing the pink gum colour.

By varying the nature and quantity of the pigment, the manufacturer of artificial teeth can produce almost any variety of coloured teeth, and consequently the matching of natural teeth is rendered fairly simple. Further, the dentist himself can render, when necessary, the matching still more perfect by further tinting or spotting the supplied artificial tooth with a suitable frit, and then firing at a suitable temperature, which should be lower than the temperature of firing the artificial tooth itself.

Artificial teeth are made in brass moulds, which are reproduced from plaster models made a little larger than the tooth, since the mixture from which the porcelain is produced always contracts during the firing. The moulds contain the necessary holes in which the pins, made by preference of platinum or of platinum-iridium alloy, can be inserted, the porcelain producing mixture being placed on the pins so that the latter become firmly imbedded in the porcelain. The brass moulds having been oiled and the pins inserted, the mould is lined to a suitable extent with the enamel mixture, spread by means of a spatula. The body mixture, in quantity, rather greater than that finally required, is laid, also by means of a spatula, on the pins, and the mould, which is in two parts, finally closed and heavily

pressed. The mould is then removed from the press, and having been clamped by means of an iron clamp, is heated in the stove at a temperature of about 1200° C. When the heating has been carried on for a sufficient time, the stove is allowed to cool very gradually to the ordinary temperature. The mould is then opened and the teeth dislodged from it by striking with a wooden mallet. The teeth can be trimmed to the desired size by means of suitable fine files.

In the construction of continuous gum dentures, porcelain is employed to fill in the interstices between the mineral teeth, which have been previously secured to the swaged platinum base by pure gold or gold-platinum solder. This porcelain is used to replace such deficiencies which may exist in the alveolar contour and to cover the lingual surface of the plate. The ingredients of the porcelain used for this purpose are similar to those described above, but, since it has to fuse at a temperature below that of the body of which the porcelain teeth is made, an additional amount of flux is incorporated with them. The fusing-point of the porcelain for continuous gum dentures must, however, be higher than that of the gum enamel which has to be employed with it.

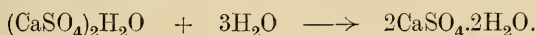
Porcelain used for ground inlays is similar in composition to that from which porcelain teeth are made. It is generally supplied in round, oval, or square-shaped rods, either straight or tapering, from which pieces are cut, these pieces being ground accurately to fit a prepared tooth cavity. A fused inlay is specially prepared for the cavity it is to fill by fusing the porcelain body in a gold or platinum matrix which has been perfectly adapted either to a model of the tooth cavity or, better, to the cavity directly. Two kinds of porcelain may be used for such inlays, viz., a high or a low fusing variety. The former fuses at a temperature higher than the melting-point of gold, while the latter fuses below this temperature. The higher fusing porcelain has a similar composition to that used for the making of artificial teeth, while the lower fusing porcelain contains relatively more flux. The matrix used for the higher fusing porcelain is made of platinum foil $\frac{1}{1000}$ th of an inch in thickness, while that for the lower fusing porcelain is made of gold. The body is mixed either with alcohol or with distilled water, and introduced into the matrix by means of a small spatula, and then fused in a muffle furnace. Owing to the shrinkage which occurs during the making of all porcelains, more than one baking is necessary. It is usual to carry the first firing to about 100° C. lower than that required to glaze the product, the full glaze being imparted at the final firing.

PLASTER OF PARIS AND DENTAL CEMENTS

Plaster of Paris was so called because it was first made by heating gypsum from the quarries of Montmartre near Paris. **Gypsum** or

selenite is hydrated calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which is found in well developed monoclinic crystals in clay in various places and, along with sulphur, in linings of volcanoes in Sicily. **Alabaster** is pure, fine-grained, massive gypsum, which is used for ornamental purposes. Calcium sulphate also occurs in the anhydrous form, CaSO_4 , in the mineral **anhydrite**, which is often found associated with gypsum and rock salt, NaCl .

When powdered gypsum of good quality, which should be free from colouring matter, is heated at a temperature of a little above 100°C ., it loses three-quarters of its water of crystallisation and becomes converted into a hydrate having the formula $(\text{CaSO}_4)_2\text{H}_2\text{O}$.¹ This hydrate constitutes **Plaster of Paris**. This substance, when made into a paste with a little water, sets to a firm mass, which gradually hardens. This product has the same composition as pure gypsum, viz., $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the setting of plaster of Paris would therefore appear to be represented as :

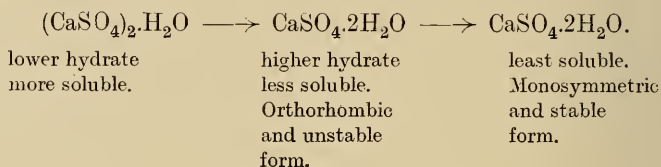


Actually, the changes involved in the setting are a little more complicated. In the first place, the hydrate $(\text{CaSO}_4)_2\text{H}_2\text{O}$ is soluble in water to a certain extent, and the saturated solution of this hydrate deposits crystals of the hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which is less soluble than the former one. Further, the crystals of the hydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, when first deposited are of an unstable form, and change into the stable form on standing. The crystals of the less stable form belong to the orthorhombic system, and they change into the more stable form which belong to the monosymmetric system. Actually then, the setting of plaster of Paris involves first the solution of a small portion of the lower hydrate to form a saturated solution, which, being supersaturated with respect to the higher hydrate, deposits crystals of the

¹ Anhydrite, i.e. anhydrous calcium sulphate, CaSO_4 , does not set when mixed with water. When gypsum is heated to a temperature somewhat above 200°C ., when it has lost all its water of crystallisation, the product is described as being "dead-burnt," and then, like anhydrite, does not set when mixed with water. Although this anhydrous calcium sulphate does become hydrated, it does not set like plaster of Paris, and this may be explained by the existence of two forms of calcium sulphate, which persist also through the two hydrates.

Some plaster of Paris cements are, however, made at temperatures above 200°C ., e.g. Keene's cement and Parian cement. According to the English patent, 1838, Keene's cement is made by calcining pure gypsum at a red heat, then immersing in an aqueous solution of potash alum, drying and recalcining at a high temperature. The product is then finely ground. Parian cement, according to the English patent, 1846, is made by dissolving 5 lbs. of borax in 6 gallons of water, and mixing this with a solution of 5 lbs. of cream of tartar (potassium hydrogen tartrate) in 6 gallons of water. The gypsum is immersed in this, then calcined, and the product carefully ground. These two cements, and especially the latter, are of value in dental work.

latter in the unstable form, which gradually change on standing into the stable monosymmetric variety. These changes then go on progressively, provided sufficient water is present, through the entire mass. Thus :



The change from the unstable, orthorhombic higher hydrate to the stable, monosymmetric hydrate is accompanied by expansion, and this expansion is of great importance in taking plaster casts, as the plaster fills the mould completely when finally set. The formation of the intermediate unstable and therefore more soluble orthorhombic form affords an explanation of the holding together of the solid product. The inner portions of it are filled with minute interlacing crystals which have separated from a solution saturated with the unstable form, and therefore supersaturated with respect to the stable form. Apart from expansion the combination of plaster of Paris with water is accompanied by a small but noticeable evolution of heat.

Plaster of Paris is used in dentistry for the construction of models of the teeth and contiguous parts, as an investing material in the processes of vulcanising and soldering, and for taking impressions of the mouth. The plaster used for taking impressions is usually ground more finely than that employed as an investing material and for making casts. In this condition it sets more rapidly, but is not quite so strong and therefore more suitable for the purpose, as it fractures easily and facilitates the withdrawal of the impression from the undercut spaces. The proportions of plaster to water usually employed are five to three by weight. In mixing, the plaster should be added to the water, and not vice versa. It is usual to sift the plaster into the water and allow it to become saturated as it slowly sinks to the bottom of the vessel. In this manner "air blows" are avoided, and the surplus water can be poured off and the mass thoroughly stirred with a broad spatula. The setting may be hastened by the use of warm water, or by employing a 6 per cent. aqueous solution of sodium chloride or potash alum instead of pure water. It is stated that such salts render the product more brittle, which is of advantage when securing impressions of marked undercut spaces.

When plaster is confined in a mould during setting it tends to rise whilst expanding. The result is that the surface in contact with the bottom of the mould becomes arched, the mass being free to rise at the centre of the exposed surface, but is held down somewhat by the

sides of the mould. The same result is seen when plaster is used as an impression material. The impression tray acts as a mould, and there is often some rising of the mass in the palatal region of the impression. The chief advantages of plaster as an impression material are :

(a) It copies exactly the teeth and contiguous soft tissues without displacing the latter.

(b) Although it cannot be withdrawn from undercut spaces without fracture, its lines of fracture are so sharp and clean as to permit of the broken fragments being easily pieced together again.

While the expansion which plaster of Paris undergoes on setting, and which is complete after twelve hours, is not large, the errors due to the use of plaster as an impression material are important. The changes in volume which plaster undergoes on setting, under various conditions, have been carefully investigated by Simms.¹ Simms shows quite clearly that not only does plaster expand on setting, but increased mixing actually increases the expansion. When a 6 per cent. solution of sodium chloride is used instead of water for the mixing, the time of setting is reduced to one-third approximately, but the effect on the expansion is negligible, and similar effects are noticed when a dilute solution of potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) is employed. On the other hand, aqueous solutions of potassium sulphate, and especially sodium potassium tartrate (Rochelle salt) and sodium tartrate, not only reduce the time of setting, but also reduce the expansion. When a solution containing 40 grains of the tartrate in $1\frac{1}{2}$ ounces of water was employed to $2\frac{1}{2}$ ounces of plaster, the time of setting was actually reduced to about one-half, while the expansion was actually one-fiftieth of its normal value, and so became negligible in practice. It is not certain whether the increased density of the set plaster so produced accounts for the diminution in the expansion, but the experimental results are very striking. The presence of such salts weakens the plaster, but this is no disadvantage for impression work.

Plaster of Paris itself, or such a plaster as described by Simms, is not suitable for the making of casts which have to be subjected to considerable heat changes and pressure. The so-called "Spence's Plaster Compound" is, however, an excellent material for such work. It is essentially a mixture of plaster of Paris and Portland cement, and is typical of a number of the so-called investment compounds placed on the market.

Portland cement is made by calcining a mixture of limestone (calcium carbonate, $CaCO_3$) and clay. Under these conditions a complex mixture of calcium aluminates and calcium silicates containing an excess of lime is produced. When this is finely ground and mixed with water it sets in the course of a short time to a hard

¹ *British Dental Journal*, 42, 1921, 425.

mass, the hardness actually increasing over a long period (see below).

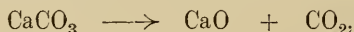
The mixture of plaster of Paris and Portland cement has, according to Wilson,¹ four times the strength of dental plaster, and the expansion is negligible. It naturally requires less water than pure plaster of Paris, and when mixed, should be of a putty-like consistency which can be kneaded with the fingers. It requires to be well packed and jarred in filling the impression.

In preparing a plaster cast from an impression it is necessary to treat the surface of the latter with some preparation which, while preventing the adhesion of one to the other, shall in no way alter or injure the surface of the cast. The common practice of coating the surface of the impression with soap solution, or with oil or vaseline, is not recommended. These substances soften the face of the cast and tend to produce air blows. A better method is to paint the surface of the thoroughly dried impression with a solution of one part of shellac resin in eight parts of alcohol. This penetrates the impression and imparts a brownish colour. When the painted impression is quite dry a further coat of a solution of one part of sandarac resin in eight parts of alcohol is applied in a similar way. When dry, the surface of the impression is hard and perfectly smooth, and the reproduction of a good cast is ensured.

DENTAL CEMENTS

The cements used in conservative dentistry either as temporary filling materials or as cavity linings can be divided into two chief classes: (a) silicate cements, and (b) basic salt cements.

(a) The **Silicate Cements** are of the nature of very fine Portland cement made in various ways, which are trade secrets. Portland cement is made by heating together a finely ground mixture of calcium carbonate and clay (see p. 84), the purest materials being employed.² During the heating the calcium carbonate is decomposed,



and the lime so produced combines with both alumina and silica from the clay, forming a mixture containing free lime, calcium aluminates and calcium silicates. The actual composition of the latter compounds is still not known with certainty. It is possible that at any rate they contain tricalcium aluminate, whose composition may be represented as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$. When the finely ground product is mixed with water it sets to a solid mass

¹ *Dental Prosthetics*, 4th edition, 1920, p. 138.

² Portland cement, largely used as a building material, is generally made of comparatively crude materials, and is usually mixed with such material as sand and stone beside water, and when the mass sets it forms *concrete*.

similar to, but stronger than, plaster of Paris, which gradually grows harder. When once it has set such a cement is a very resistant material, even when water is continually present. Obviously the use of such a similar silicate cement in dentistry possesses many advantages; it matches the tooth substance very closely, and although a silicate cement is somewhat irritating, this can be reduced in practice by lining the cavity with the adhesive zinc oxyphosphate before insertion of the silicate filling. The resistance of such a silicate cement to chemical action is also a strong recommendation for dental purposes.

In his highly instructive paper, "The Translucent Filling Cement," Doubleday¹ describes the constitution of typical silicate cements in common use. The powder consists essentially of a fine Portland cement, and this is mixed with a solution of phosphoric acid, which may contain zinc or aluminium phosphate in solution. Lowry, contributing to the same paper, compares the setting of Portland cement with that of the dental silicate cements as follows:

"In the case of Portland cement the decomposition by water of calcium silicates and aluminates containing an excessive proportion of lime is probably the fundamental change, but the actual mechanism of the setting and the extent to which colloidal material plays a part in it appear to be still matters of controversy."

"In general, the properties demanded of dental cements are similar to those which are essential in Portland cements used for constructional work, the two most important properties being (1) hardness, which in this case must take the form of 'edge strength,' and (2) smallness of change of volume in setting, which, in the case of a dental cement would produce a loose filling if there were a substantial contraction, and a split tooth if there were a substantial expansion. A principal point of difference is found in the fact that a higher rate of setting is required in a dental cement, since, whilst the boarding of a concrete structure may conveniently be kept in position for a day or more, these conditions can scarcely be applied to the insertion of a stopping in a tooth."

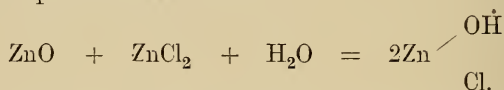
Regarding the mechanism of setting Lowry states that silicate cements are those "in which various silicates and various salts of aluminium are converted into phosphates by the action of an aqueous solution of phosphoric acid, sometimes saturated with aluminium or zinc phosphate."

Zinc Oxide, ZnO , is the basis of the formation of the osteo-cements, which are actually basic salts. Zinc oxide is used to a very considerable extent in the making of white paint, under the name of "zinc white." This material is produced commercially by distilling zinc in a current of air or steam. For pharmaceutical purposes it is

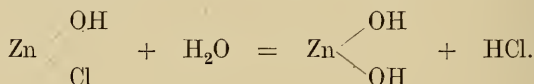
¹ *The Dental Record*, 1929, 40, 551; compare Voelker, *The Place of the Silicates in Dentistry*, Dental Summary, 1916, 177.

produced in a purer form by igniting the carefully purified basic zinc carbonate which has been precipitated by adding an aqueous solution of sodium carbonate to an aqueous solution of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Zinc oxide, which is white at ordinary temperatures, has the characteristic property of becoming yellow on heating, the yellow colour disappearing again on cooling.

When zinc oxide is mixed with a solution of zinc chloride, the mixture sets to a hard mass of zinc oxychloride. The reaction taking place may be represented as follows :

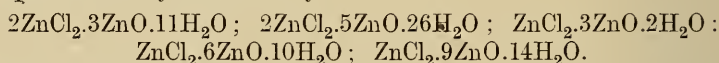


The use of this basic chloride, produced in the manner described, as an osteo-cement has now been largely abandoned, since it has an irritant action on the tooth substance. This irritant action is probably due to the oxychloride slowly undergoing further hydrolysis with the production of hydrochloric acid according to the following reaction :



Since normal saliva is alkaline, and may become acid during ill-health, the disintegration of such a substance as zinc oxychloride in the mouth will be more rapid even than when it is in contact with pure water.

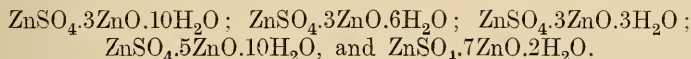
It should be remarked that the product formed by mixing zinc oxide in a solution of zinc chloride does not necessarily have the composition represented by the simple formula, $\text{Zn}(\text{OH})\text{Cl}$. A large number of basic zinc chlorides are known, and the following formulæ, which have been assigned to some of them, indicate clearly that their compositions vary considerably :



It is clear, therefore, that the composition of the oxychloride, prepared under the conditions described above, will vary according to the relative amounts of zinc oxide, zinc chloride, and water present, and also according to the temperature conditions during the mixing. It is not at all improbable that the actual product used as a cement may be a mixture, the setting of which may be explained by a similar hypothesis to that set forth for explaining the setting of plaster of Paris and the silicate cements.

The basic zinc sulphates (zinc oxysulphates) are of an analogous nature to the zinc oxychlorides. As an osteo-cement zinc oxysulphate is prepared in a similar manner to that in which zinc oxychloride is prepared; a solution of zinc sulphate, usually containing a little

gum-arabic, is employed in place of zinc chloride solution. As in the case of the basic zinc chlorides, numerous zinc oxysulphates are known, but they have not been investigated so thoroughly. The following formulæ represent the compositions which have been assigned to some of them :



These basic zinc sulphates, as osteo-cements, suffer from the same defects, and for the same reasons, as the basic zinc chlorides.

Although much less is known about them from a chemical point of view, the zinc oxyphosphates (or basic zinc phosphates) are used much more extensively nowadays than either the basic chlorides or basic sulphates. The chief use of zinc oxyphosphate is as an adhesive for lining the prepared cavity before inserting a silicate or amalgam filling. It is made by mixing the zinc oxide in a solution of phosphoric acid, the quantity of zinc oxide used being greater than that required to neutralise the phosphoric acid. Zinc oxyphosphate is preferred to the oxychloride¹ and oxysulphate. It is antiseptic almost to the same extent, and, while it does undergo disintegration for the same reasons, it lasts for a much longer time. Moreover, it is distinctly less irritating to the tooth-substance.

¹ It is interesting to note that magnesium oxide when mixed with a solution of magnesium chloride forms a cement (Sorel's cement), which is very similar to, but harder than, the corresponding zinc oxychloride. This cement is now finding extensive use as an artificial stone, for which purpose it is worked up with such materials as sawdust and cork. This artificial stone wears extremely well, and highly artistic effects can be produced when it is suitably manipulated.

CHAPTER XV

ABRASIVE MATERIALS

It is scarcely necessary to point out the importance of the use of suitable materials for grinding and polishing in conservative and prosthetic dentistry. The processes of grinding and polishing may be considered almost as one process, polishing being generally the final stage of grinding. As a general rule, grinding materials have a hardness greater than the surface to be ground, in order to act effectively and speedily; but the materials used for polishing are, in most cases, less hard than those used for grinding, so as to avoid cutting too far into the surface being treated. In grinding and polishing, therefore, it is customary to employ a series of abrasives in diminishing order of hardness so that they exercise a regularly diminishing action, the object being to leave the surface finally as smooth as possible. To some extent, the same effect may be obtained by using the same abrasive all the way through, but with diminishing intensity and with increasing degree of fineness. A polishing material may be, and frequently is, much softer than the surface to be polished, but its application at a considerable pressure produces the necessary effect of hardness. For example, cloth mounted on wheels which revolve at high speed proves a very effective and frequently used polishing material, especially when the cloth is impregnated with a material such as rouge.

Although it is somewhat difficult to define exactly the meaning of "hardness" when applied to materials, a substance A is described as being harder than substance B if when A and B are rubbed against each other, B is scratched and not A. Hardness can be tested by drawing a sharp corner of the one substance along a smooth surface of the other, and, since the scratch made is a line along which the particles have been thrust asunder until their cohesion has been overcome, hardness obviously depends on the degree of cohesion of the particles of a substance.

For minerals, Moh has devised a scale of hardness of mineralogical substances as follows:

SCALE OF HARDNESS

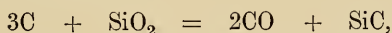
- | | |
|--------------------------|----------------------|
| 1. Talc | 6. Orthoclase. |
| 2. Gypsum and rock salt. | 7. Quartz. |
| 3. Calcite. | 8. Topaz. |
| 4. Fluor spar. | 9. Corundum (emery). |
| 5. Apatite. | 10. Diamond. |

A substance which can scratch fluor spar, but not apatite, would be described as having a hardness of between 4 and 5, and, although such an estimation of hardness is merely an approximation, it serves as a useful means of classification of materials according to their "hardness." A rough idea of the relative hardness of a substance may be gained after a little experience by seeing how readily or otherwise it may be scratched by means of a penknife blade, which is then regarded as the standard substance.

Apart from the metallic substances (varieties of steel) used for drills of various sizes employed in the preparation of teeth cavities, etc., a number of hard mineral abrasives, such as diamond powder, carborundum, corundum (emery), and sand are employed as grinding materials. Such materials form the important part of grinding wheels, which, when suitably mounted, can rotate at a high speed and be kept cool by means of water. The binding material for the construction of such grinding wheels is siliceous material, which is very viscous when fused so as to hold the abrasive particles firmly, and does not become polished in operation. A material made from finely ground felspar and a smaller portion of an easily vitrifiable clay is suitable. The softer, or mild mineral, abrasives, which form what are usually known as polishing powders, are usually chalk, rouge, pumice, kieselguhr, Tripoli powder, and putty powder.

Diamond, the characteristic crystalline and purest form of naturally occurring carbon, is used in the form of fragments of coarse powder. It is the hardest substance known, and has a hardness of 10 on Moh's scale. The larger fragments of diamond are held in a suitable clamp, and employed as cutting tools (*e.g.* glass cutters), and the smaller fragments (or powder) are applied to the surface to be ground under pressure in the presence of water.

Carborundum, or silicon carbide, SiC , is a highly crystalline material possessing a hardness approximating very closely to that of diamond. This material is manufactured on a very large scale, chiefly at Niagara Falls, by heating together a mixture of silica, SiO_2 , in the form of quartz, and carbon, in the form of coke, in electric furnaces. The formation of the crystalline carborundum is said to take place at a temperature of about 1800°C .



and when carborundum is heated to a temperature of about 2200°C ., it is decomposed without melting into silicon and graphite.

When pure, carborundum forms masses of colourless, lustrous hexagonal crystals; but the commercial product is usually coloured, its colour varying from yellow to greenish-gray, and even almost black. On Moh's scale its hardness is about 9.5. It is remarkable not only on account of its hardness and infusibility, but also on account of its resistance to most chemical reagents. Fused alkalis (sodium

and potassium hydroxides) decompose it, producing silicates and carbon.

Mounted with a suitable binding material in the form of grinding wheels, it is used extensively for grinding and polishing metal, porcelain, glass, precious stones, etc. Carborundum powder, left from the crushing of carborundum as produced in the electric furnace, is used in the manufacture of steel as a source of silicon and carbon.

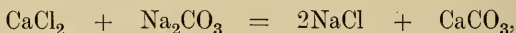
Corundum is aluminium oxide, Al_2O_3 , of which the ruby, sapphire, and emery are naturally occurring varieties. **Emery** is the least pure form, and the natural variety, found in the Greek island of Naxos and in America, contains, besides alumina, iron oxide and other minerals. The grinding power of emery is dependent on the proportion of corundum (hardness 9 on Moh's scale) it contains, and consequently what is known as artificial emery, which contains generally a very much higher proportion of alumina, has become of very great importance as an abrasive material. One variety of artificial emery is known as **alundum**, and is made by fusing bauxite (see "Aluminium") in an electric furnace. Another variety, known as **corubin**, is the by-product in thermite welding.

Emery as an abrasive is mounted not only in the form of grinding wheels, but, by means of suitable adhesive materials, on paper. It is also used in powder form like diamond.

Sand, as already stated, is impure silica, SiO_2 . For abrasive purposes it is used in its natural form and as sandstone. In the presence of water, sand makes an excellent abrasive material for metals and glass. It is also used as "sand blast" in finishing complex surfaces such as those of ornamental building materials. What is known as **glass paper** is made with quartz (hardness 7 on Moh's scale) grains in a similar manner to that in which emery paper is made.

The following are the more important mild abrasive materials or polishing powders:—

Chalk, calcium carbonate, CaCO_3 , preferably prepared by precipitation by adding an aqueous solution of a soluble carbonate to a solution of a calcium salt,



is an extremely mild abrasive, and is used largely in the manufacture of dentifrices.

Rouge is extremely fine iron oxide, Fe_2O_3 , which may be prepared by precipitating ferric hydroxide and subjecting it to ignition and final separation from the heavier particles by levigation. It is chiefly employed as a final polishing material, its softness and freedom from grit making it especially useful for this purpose.

Putty Powder is chiefly stannic oxide, SnO_2 , the best variety of which is formed by heating strongly the product obtained by acting on tin with concentrated nitric acid. For use as a polishing material

the product is ground and finally separated from heavier particles by levigation.

Tripoli Powder is usually a mixture of aluminosilicates of variable composition. One variety, known as **rottenstone**, is found near Bakewell in Derbyshire. This is usually brown in colour owing to the presence of iron oxide, Fe_2O_3 .

Pumice, which is used either in the form of powder or as **pumice stone**, is described as a frothy form of volcanic glass. It is a highly silicious material containing, probably as silicates, aluminium, iron, calcium, magnesium, sodium, and potassium. Powdered pumice has a density of about 2.4, but, on account of its cellular structure, pumice itself floats on water. It is the cellular structure on which the abrasive properties of pumice depend. Powdered pumice is used in the making of metal polishes and scouring soaps, and is often mistaken for kieselguhr.

Kieselguhr, usually white or gray in colour, is a fine powder, composed chiefly of hydrated silica, together with smaller amounts of the oxides of aluminium, iron, and calcium. It is described as a diatomaceous earth, and consists, in fact, of the silicious shields of diatomaceæ or fossil diatoms. As an abrasive material it should be free from all gritty particles, and is used for polishing metallic and other surfaces. It can be readily distinguished from powdered pumice, with which it is often confused. Under the microscope pumice appears as irregular glassy fragments, while Kieselguhr shows the regular shape of diatoms. Kieselguhr, consisting largely of hydrated silica, is, unlike pumice, soluble in a solution of sodium hydroxide.

Apart from its use as a mild abrasive or polishing material, kieselguhr, on account of its highly absorbent nature, is extremely valuable as an absorbent of nitro-glycerine in the manufacture of dynamite.

CHAPTER XVI

ANÆSTHETICS AND ANTISEPTICS

ANÆSTHETICS

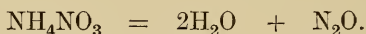
Nitrous Oxide

IN dental surgery, where operations are usually of a minor character, the most important anæsthetic is the gas, nitrous oxide, the oldest and safest of anæsthetics. The gas was discovered by Priestley in 1772, and it was Sir Humphrey Davy, in 1798, who first noticed that, when a mixture of nitrous oxide and oxygen is inhaled, it produces a condition somewhat resembling alcoholic intoxication, accompanied by hilarity and involuntary laughing, and hence the name 'laughing gas' was popularly used for the substance. Wells, in 1844, noticed that persons, under the influence of the gas, on falling did not experience pain, and this suggested to him the anæsthetic properties of the gas; but Davy had noticed this some forty years earlier, and his suggestion that nitrous oxide should be used as an anæsthetic in surgical operations passed unnoticed.¹ An interesting account of the history and use of nitrous oxide in dental practice is given by Pinson.²

Nitrous Oxide, N_2O , can be produced by the action of reducing agents on nitric oxide (NO). Priestly obtained the gas by using moistened iron filings,



and other reducing agents, *e.g.* stannous chloride, $SnCl_2$, may be employed. Somewhat later, Berthollet discovered that the gas was readily obtained by heating ammonium nitrate, the decomposition beginning at about $170^\circ C.$, becomes almost explosive on rapid heating,



This reaction is the one generally employed in the commercial production of the gas, although patents have been taken out which describe the production of the gas by reduction of nitric acid, and also by the direct combination of nitrogen and oxygen under care-

¹ "As nitrous oxide, in its extensive operation, appears capable of destroying physical pain, it may probably be used with advantage during surgical operations in which no great effusion of blood takes place" (Davy).

² *British Dental Journal*, 1921, 42, 529.

fully controlled conditions. It is very important to use pure ammonium nitrate. The presence of organic impurities gives rise to carbon dioxide, while contamination of the nitrate with ammonium chloride would cause the production of chlorine. If the temperature of the reaction is too high, nitrogen, ammonia (NH_3), and the highly poisonous nitric oxide (NO), are produced. The gas must be purified by passing through (a) a solution of ferrous sulphate, which combines with any nitric oxide present in the gas, (b) a solution of a suitable alkali, such as potassium or calcium hydroxide, so as to free the gas from any carbon dioxide.

In order to moderate the reaction, the ammonium nitrate may be mixed with sand, or a mixture of potassium or sodium nitrate and ammonium sulphate used instead of preformed ammonium nitrate,

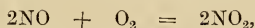


After scrubbing, the gas may be dried either with an emulsion of ferrous sulphate and concentrated sulphuric or with concentrated sulphuric acid alone. The gas is transported in small steel cylinders, which contain the gas under pressure, and from which the gas can be obtained through a regulating valve.

Properties of Nitrous Oxide.—Nitrous oxide is a colourless gas with a sweetish taste. One litre of the gas at 0°C . and 760 mm. pressure weighs 1.9774 grams, and its density is 1.5297 (air=1). Water dissolves rather more than its own volume of nitrous oxide at 5°C ., and the solubility of the gas in water rapidly diminishes at higher temperatures. The gas is more soluble in blood than in water; it is probably taken up by the lipoids of the corpuscles in a similar way to chloroform. Nitrous oxide is described as an endothermic compound, *i.e.* its formation from nitrogen and oxygen, which has been shown to be possible, is accompanied by an absorption of heat.

Priestley showed that nitrous oxide is an active supporter of combustion, and that substances such as carbon, sulphur, phosphorus, and a candle burn almost as well in it as they do in oxygen.¹ Further, nitrous oxide is decomposed into its constituent elements on being strongly heated. Although nitrous oxide is therefore easily decomposed chemically, it is not decomposed in the human body, the tissues of which exposed to it suffer from asphyxia, owing to lack of oxygen or air. Plants do not grow and seeds do not germinate in nitrous oxide. Animals die in nitrous oxide in almost the same time as they do in an indifferent gas like hydrogen or nitrogen, and at death their

¹ Nitrous oxide can be readily distinguished from oxygen by the fact that it does not react with nitric oxide. Nitric oxide mixed with oxygen produces the brown nitrogen dioxide gas, a diminution in volume taking place,



the volume of the nitrogen dioxide produced being identical with that of the nitric oxide, the temperature and pressure remaining the same.

blood contains no oxyhæmaglobin, proving conclusively, that nitrous oxide does not support combustion in the animal body.

A person inhaling a mixture of 4 parts of nitrous oxide and 1 part of oxygen by volume, experiences a rushing, drumming, and hammering sensation in the ears, indistinct sight, and a feeling of warmth and comfort. Sensibility to pain is distinctly less, but with such a mixture anæsthesia is not complete. With pure nitrous oxide (*i.e.* without oxygen), the above sensations are passed through rapidly, and loss of consciousness takes place. The face becomes cyanotic, and in a short time the breathing becomes laboured, and finally ceases after a weak convulsion. If the mask covering the nose and mouth (the usual method of administration) is removed when cyanosis has set in, complete anæsthesia continues for about half a minute, and the patient recovers in a very few minutes without suffering any after-effects whatever. In practice, inhalation is carried on until distinct cyanosis occurs, when anæsthesia lasts sufficiently long to permit of the performance of short operations. The greater safety of the use of nitrous oxide above other anæsthetics has led to the extension of its use in cases of more lengthy operations; in these cases, nitrous oxide-oxygen mixture is administered in conjunction with a local anæsthetic.

Nicloux has determined the approximate concentrations of nitrous oxide in the blood during various stages of anæsthesia. His results were as follows:—

Beginning of anæsthesia,	concentration of N_2O	= 0.040 g.	per 100 c.c. of blood.
Deep anæsthesia,	„ „	= 0.050 g.	„ „ „
At death,	„ „	= 0.060 g.	„ „ „

Cushny states,¹ “Nitrous oxide has a special effect on the central nervous system; although in the rest of the tissues it acts only by excluding oxygen; it depresses the brain by virtue of its molecular form just as chloroform or ether does.” Again on page 230, “The anæsthesia is due to a specific action on the nervous tissues, although this may be reinforced by the asphyxia present.” For further details regarding its action on the nerve cells, the respiratory centre, and on the circulation, the work mentioned should be referred to.

CHLOROFORM, ETHYL CHLORIDE, AND ETHER

If the dental operation is likely to be more prolonged than one that can be done using nitrous oxide as the anæsthetic, the anæsthetics administered by the anæsthetist are chloroform or ether, or suitable mixtures of these. Ethyl chloride has also been used during recent years as an anæsthetic, more especially for minor operations.

The use of ether as an anæsthetic was advocated about 1840-1850

¹ *Pharmacology and Therapeutics*, seventh edition, p. 229.

by Long, and by Jackson and Morton. In 1847, Simpson introduced the use of chloroform as a substitute for ether, over which he claimed it possessed many advantages. It was not until after chloroform and ether were in general use as anæsthetics that nitrous oxide began to be largely employed for short operations.

Chloroform and ether are given by inhalation, by which method the degree of narcosis can be easily controlled by the anæsthetist. According to Cushny (*l.c.*, p. 202) the action of chloroform and ether on the central nervous system is very similar to that of alcohol. In the case of all three intoxicants, the stages of lessened consciousness, excitement, and complete unconsciousness are observed. It is interesting to note that alcohol was formerly administered in large quantities to allow of the performance of surgical operations, and ether has been used as an habitual intoxicant. Chloroform and ether are not chemically changed in the body, and are excreted chiefly by the lungs.

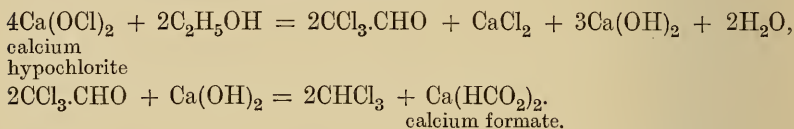
Chloroform is carried for the most part by the red corpuscles of the blood, the concentration in the plasma being very much less than that in the red cells. On the other hand, ether is found to be much more equally distributed between the corpuscles and the plasma.

The amount of chloroform in the blood during anæsthesia is stated to be 0.025 to 0.035 gram per 100 c.c., and Buckmaster and Gardner¹ find that when respiration ceases, the chloroform content is 0.040 to 0.70 gram per 100 c.c. During inhalation arterial blood contains more chloroform than the venous blood, and during recovery the reverse is the case. Nicloux has determined the ether content of blood during various stages of anæsthesia produced by ether. He finds that during light anæsthesia the blood contains 0.100 to 0.110 gram per 100 c.c., in deep anæsthesia 0.130 to 0.140 gram, and at failure of respiration the concentration is 0.160 to 0.170 gram per 100 c.c.s. of blood. On inhalation, chloroform or ether vapour diffuses rapidly into the blood, and becomes distributed throughout the body. The anæsthetic leaves the blood and is taken up by the tissues, especially by the central nervous system, in which it is found during the induction of anæsthesia in larger quantities than in the muscles, liver, or blood. This is probably due to the greater amount of lipoid substances in the central nervous system which dissolve the chloroform and ether and retain them. This unequal distribution lasts until equilibrium has set in, and then the vapour tension is the same in each, and the amount of anæsthetic in the brain is then determined by the amount in the blood. The pharmacological action of chloroform and ether has been carefully studied, and a comprehensive account is given by Cushny (*loc. cit.*).

¹ *Proc. Roy. Soc., B.*, 78, 79, 84, p. 341: compare Gibson and Laidlaw, *Guy's Hospital Reports*, 1922, p. 359.

Chloroform, CHCl_3 , trichloromethane, is one of the chlorine substitution products of methane, CH_4 .

It is manufactured commercially by heating together ethyl alcohol and bleaching powder at a maximum temperature of 60°C . The action which takes place is a complex one, and probably consists in the formation of chloral (trichloroacetaldehyde), CCl_3CHO , by oxidation of the alcohol to acetaldehyde, and subsequent chlorination of this, and then decomposition of the chloral by means of the calcium hydroxide present in the bleaching powder. Omitting intermediate stages, the reaction may be formulated,



The chloroform which distils over contains ethyl alcohol, ether, and a small quantity of acetaldehyde. When the chloroform has to be used as an anæsthetic, it is washed successively with distilled water, with dilute sulphuric acid, with dilute sodium hydroxide solution, and finally with distilled water. Finally, it is dried by standing with fused calcium chloride and carefully redistilled. It should boil at 61.2°C ., and the pure chloroform is mixed for anæsthetic purposes with 2 per cent. of pure (absolute) ethyl alcohol.

Acetone, $\text{CH}_3\text{CO}\cdot\text{CH}_3$, may be substituted for ethyl alcohol in the manufacture of chloroform, the reaction being carried out in much the same way. In Besson's process, which is stated to be almost quantitative, for the manufacture of chloroform, the alcohol is first chlorinated by dry chlorine gas and the chlorinated alcohol is then warmed with milk of lime or sodium hydroxide. Chloral, or chloral hydrate, $\text{CCl}_3\text{CHO}\cdot\text{H}_2\text{O}$, or some similar compound is present in the chlorinated alcohol, and when this is heated with the alkali pure chloroform distils over,

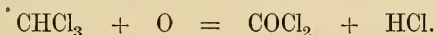


The product obtained by heating pure chloral with sodium hydroxide is very pure. Chloroform may be purified by crystallisation below -70°C . (Pictet), and Auschütz's method consists in heating the crude chloroform with the substance, tetrasalicylid ($\text{C}_7\text{H}_4\text{O}_2$)₄, when a crystalline compound separates ($\text{C}_7\text{H}_4\text{O}_2$)₄·2 CHCl_3 , which can be separated. This compound on being heated gently gives up its chloroform, which distils over in a pure state, leaving the tetrasalicylid behind, which can thus be used repeatedly.

Physical and Chemical Properties of Chloroform.—Pure chloroform is a colourless, highly refractive liquid, which has a sweet taste and an agreeable ethereal odour. It has a boiling point of 61.2°C ., and it melts

at -63.2° C.; its density at 0° C. is 1.5264 compared with water at 4° C.

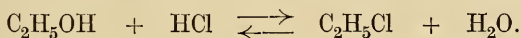
Chloroform is not inflammable; its vapour imparts a green colour to the colourless flame. When exposed to air and sunlight chloroform undergoes decomposition, hydrochloric acid and chlorine being set free in small quantity. Chloroform which may have undergone slight decomposition is not suitable for anæsthetic purposes, since the products of the decomposition, although present in small quantities, have a deleterious and poisonous action. Such chloroform can be readily purified by shaking with sodium thiosulphate solution, and after washing and drying, it should be distilled. It has been shown that the addition of 2 per cent. of absolute or pure ethyl alcohol to pure chloroform prevents this decomposition, and chloroform for anæsthetic purposes always contains specially added alcohol. As an additional precaution, chloroform should always be kept in tightly stoppered bottles and stored away from the light. It is usual to use coloured bottles for storing chloroform. Another decomposition which occurs when chloroform is evaporated in the neighbourhood of large flames, results in the formation of hydrochloric acid and carbonyl chloride or phosgene, COCl_2 ,



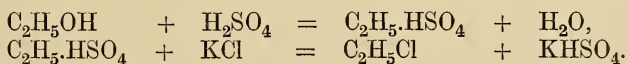
Phosgene is one of the most poisonous gases known; one volume in 40,000 volumes of air is sufficient to induce pulmonary œdema if inhaled for thirty minutes. The œdema, which comes on slowly, proves fatal only after some hours. Hence there is some danger to patients and attendants in small operating theatres where there are naked flames, and accidents have been recorded from this cause.

Chloroform used for inhalation should be neutral to test-paper, and when shaken up with water the latter should show neither the presence of chlorine (potassium iodide-starch paper) nor hydrochloric acid (silver nitrate solution).

Ethyl Chloride, monochloroethane, $\text{C}_2\text{H}_5\text{Cl}$, may be obtained by passing dry hydrogen chloride into ethyl alcohol in the presence of zinc chloride, which takes up the water formed during the reaction,



It is manufactured by mixing concentrated sulphuric acid with alcohol, and, after standing, the mixture is somewhat diluted with water, potassium chloride added, and distilled. The reactions may be formulated,



Properties of Ethyl Chloride.—Ethyl chloride is a gas at the ordinary temperature and pressure. It has a boiling point of 14° C.,

and solid ethyl chloride melts at -141.6°C . It is supplied condensed as a colourless liquid in special tubes, from which the liquid can be obtained as required.

It is liable to contain the same impurities as may be present in impure chloroform. On evaporation, ethyl chloride produces a considerable lowering of temperature, and for this reason it finds employment as a local anæsthetic, in addition to its use as a general one. Its use in dentistry is chiefly that of a local anæsthetic by spraying it on to the surface to be operated upon. On account of its low boiling point, the rapid evaporation produces so great a cooling as to cause local anæsthesia. It is not unlikely that other low boiling substances might prove useful for the same purpose.

Ether, diethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, may be considered to be derived from ethyl alcohol by taking away water according to the following equation,



It is manufactured by heating a mixture of ethyl alcohol and concentrated sulphuric acid, and subsequently adding alcohol to the heated mixture when the ether with by-products distils over. The reaction goes in two stages, the first one of which consists in the production of ethyl hydrogen sulphate,



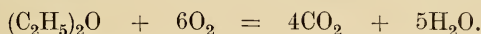
Theoretically, there is no loss of sulphuric acid, and the process may be regarded as a continuous one. In practice, however, loss of sulphuric acid does take place, owing to its oxidising action on ethyl alcohol, and consequent reduction to sulphur dioxide, and, in any case, the above equations indicate that the sulphuric acid becomes diluted, and then would cease to be effective. The crude ether prepared by this process is liable to be contaminated with ethyl alcohol, which to some extent distils over unchanged with it, with sulphur dioxide and acetaldehyde, owing to the reduction of sulphuric acid and oxidation of ethyl alcohol, and with water. These are got rid of by shaking up with dilute sodium hydroxide solution and then washing with water, followed by drying with fused calcium chloride and subsequent distillation.

The catalytic dehydration of ethyl alcohol, by passing ethyl alcohol vapour over heated aluminium oxide, Al_2O_3 , or kaolin, has now become a commercial method for the production of ether. The crude ether so obtained is much purer than in the above process, and its subsequent freeing from ethyl alcohol and water is comparatively easy.

Physical and Chemical Properties of Ether.—Ether is a colourless liquid, boiling at 34.6°C ., and having a density of 0.7191 at 15°C ., compared with water at 4°C . It is partly soluble in water, and water

also dissolves ether so that the two liquids are partially miscible with each other.

It is highly inflammable, and its vapour forms an explosive mixture with air or oxygen. The products of combustion are carbon dioxide and water,



Apart from its inflammability, it is a remarkably stable substance. Still, in the presence of sunlight and oxygen (air), it does become oxidised to a small extent, and ether stored in bottles, especially when the bottles are not completely full, has been found in the Tropics to contain unstable peroxides and acetaldehyde. The presence of these substances renders ether irritating to the mucous membranes.

When used for anæsthetic purposes, ether should not be acid in action to litmus, and when shaken up with potassium hydroxide should not be coloured brown by the formation of aldehyde resin. It should, on account of its inflammability, be stored in a cool place and away from any flames.

What is known as "A.C.E." mixture consists of ethyl alcohol 1, ether 2, and chloroform 3 parts by volume. This mixture has been advised as an anæsthetic. The use of such a mixture cannot be recommended on account of the differences in the volatilities of the constituents. In using such a mixture the anæsthetist is naturally very largely in ignorance of the nature of the anæsthetic he is administering at a particular time. The same criticism applies to the use of the other mixtures of anæsthetics which have been proposed from time to time.

LOCAL ANÆSTHETICS

The use of ethyl chloride as a local anæsthetic has already been referred to. Ethyl chloride produces local anæsthesia, not in virtue of its chemical properties, but on account of its low boiling-point, and it is not improbable that other substances of low boiling-point might be found equally efficacious in this respect. On the other hand, certain substances when injected have been found to produce loss of sensation by paralysing the terminations of some of the sensory nerves, particularly those conveying impressions of pain and touch. The part into which injection has been made can therefore be cut into or subjected to surgical treatment without the sensation of pain being experienced, so long as the surgical treatment does not extend beyond the area to which the injected substance has penetrated. Substances which on injection produce this local insensibility to pain are known as local anæsthetics, and a few of such substances are employed largely in the minor operations of dental surgery.

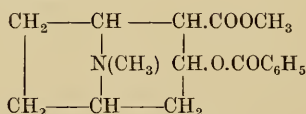
The earliest of the local anæsthetics to be investigated and employed in dental surgery is **cocaine**,¹ which occurs along with other alkaloids in the leaves of the coca plant, grown in Peru, India, and Ceylon. Cocaine is an organic base, and it is injected in the form of its hydrochloride dissolved in water. Solutions of cocaine hydrochloride do not keep well, moulds develop in them, and, since they suffer decomposition on boiling, they cannot be easily sterilised. Apart from these disadvantages, the injection of cocaine hydrochloride has often been followed by somewhat dangerous toxic effects, and, in the early days of its use as a local anæsthetic, with fatal results. The study of its chemical composition, however, led to the investigation and preparation of less dangerous substitutes. Of these, the one which has proved most useful in dental surgery is **Novocaine**,² which, like cocaine, is injected in the form of its hydrochloride in aqueous solution. Novocaine is much less poisonous than cocaine, and produces much less irritation. While its anæsthetic action is less powerful than that of cocaine, it is sufficiently lasting for most purposes, especially when admixed with adrenaline, which delays the absorption of the novocaine by the tissues.

Another substance which has been used, but only to a small extent, in dental surgery as a local anæsthetic is urea hydrochloride, $\text{NH}_2\text{CO.NH}_2\text{HCl}$. This substance is only very slowly absorbed by the tissues, and hence the local anæsthesia produced by it passes away very slowly.

ANTISEPTICS AND DISINFECTANTS

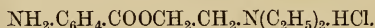
These two terms are often regarded as being synonymous, but, strictly, an antiseptic is a substance which prevents the growth of germs or bacteria so long as it is in contact with them, while a disinfectant is a substance used for actually killing the agents of infection. As might be expected, many substances may act both as disinfectants and as antiseptics, according to the relative quantities in which they

¹ Cocaine (benzoyl methyl ecgonine) has the empirical formula $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$, and its constitutional formula is :—



It is closely related to tropine, derived from atropine by hydrolysis. For further details see *The Chemistry of Synthetic Drugs*, Percy May, 1918, p. 91.

² Novocaine is the name generally given to the hydrochloride of the diethylamino derivative of ethyl-p-aminobenzoate, which has the constitutional formula :—

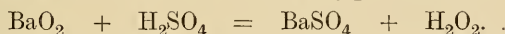


See *Chemistry of Synthetic Drugs*, loc. cit., p. 102.

are used. Until quite recently,¹ a serious limit has been placed on the use of substances as antiseptics, since few of the substances used differentiated but little in their action on the protoplasm of bacteria and that of man.

The substances used as antiseptics and disinfectants in dentistry are comparatively few in number. The inorganic disinfectants generally employed are oxidising agents, *e.g.* hydrogen peroxide in aqueous solution, iodine dissolved either in alcohol or in an aqueous solution of potassium iodide, aqueous solutions of hypochlorites, potassium permanganate in aqueous solution, and a similar solution of potassium chlorate.

Hydrogen Peroxide, H_2O_2 , is usually prepared by the action of dilute sulphuric acid on barium peroxide, BaO_2 , the latter in a fine state of division, being added gradually to the former, and the temperature maintained below 10°C . The action taking place is:—



The insoluble barium sulphate is filtered off, and the filtrate is a dilute solution of hydrogen peroxide. With suitable precautions, this dilute solution can be concentrated by evaporating under diminished pressure and the anhydrous peroxide can be finally distilled. Another way of preparing the aqueous solution of hydrogen peroxide is to pass purified carbon dioxide through cooled water in which the finely divided barium peroxide is suspended; the insoluble barium carbonate is separated by filtration.

Pure hydrogen peroxide is a colourless liquid, which freezes at -1.7°C . As obtained commercially it is in the form of its aqueous solutions, which decompose slowly according to the equation,



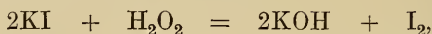
The decomposition of such solutions is facilitated by the presence of alkalis, and by contact with finely divided metals, such as platinum, and finely divided solid compounds, such as manganese dioxide. Certain substances, such as sulphuric acid, phosphoric acid, acetanilide ($\text{C}_6\text{H}_5\text{NH.CO.CH}_3$), etc., in small quantities are frequently added to solutions of hydrogen peroxide in order to minimise the decomposition, and the solutions are also frequently contained in glass bottles lined with paraffin wax so as to prevent their decomposition by the alkali, which may otherwise be dissolved from the glass.

Solutions of hydrogen peroxide are described as being "10 volumes," "20 volumes," and so on. By "10 volumes" hydrogen peroxide is meant a solution which on decomposition gives rise to ten times its volume of oxygen, according to the above equation.

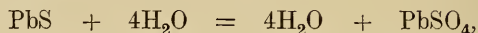
¹ The recent work on the antiseptic properties of dyestuffs, particularly those of the acridine series (flavine and its homologues), started by Browning and others (1917), indicates that this limit to the use of antiseptics may be removed in the near future as a result of investigations now being actively prosecuted.

Thus, 100 c.c. of "10 volumes" hydrogen peroxide will give off 1000 c.c. of oxygen; 100 c.c. of "20 volumes" hydrogen peroxide will give rise to 2000 c.c. of oxygen, and so on. The strongest solution of hydrogen peroxide usually obtained commercially is known as "perhydrol," and contains 30 per cent. hydrogen peroxide. One volume of this solution yields 100 volumes of oxygen.

From the ease with which hydrogen peroxide decomposes it will be readily appreciated that it is a powerful oxidising agent. It liberates iodine from potassium iodide,



oxidises lead sulphide to lead sulphate,¹



and on account of its oxidising action, it is used as a bleaching agent for straw, textiles, feathers, hair, etc.

The use of hydrogen peroxide as an antiseptic is due to its oxidising properties. Its action on healthy skin is slow, but in contact with fistulous wounds or pus it is rapidly decomposed with effervescence, which continues till the wound is cleansed or the diseased secretion destroyed. Since hydrogen peroxide gives up oxygen, leaving behind pure water, and since hydrogen peroxide itself is odourless, it possesses special advantages as a disinfectant.

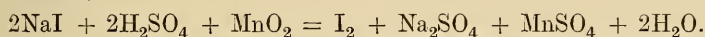
Hydrogen peroxide may be used for bleaching discoloured teeth, and "10 volumes" hydrogen peroxide (*i.e.* a 3 per cent. solution approximately) diluted with nine times its volume of water makes a very suitable liquid for cleansing the teeth and mouth generally. Hydrogen peroxide is stated to be the essential constituent of the disinfectant "sanitas."

Hypochlorites, in aqueous solution, have recently been introduced as antiseptics and disinfectants. One such solution, known as "eusol," is a solution of bleaching powder neutralised with borax (Lorrain Smith, Ritchie, and Kettle). This solution contains hypochlorous acid (HOCl), and from it chlorine is disengaged slowly and given up to the nitrogen of the proteins, thus killing the bacteria. There appears to be little evidence, however, that these hypochlorites act more strongly on bacteria than on the blood proteins, and it may be that their use for disinfecting the general tissues may be founded on error.²

¹ This reaction is made use of in restoring oil-paintings.

² Sodio-p-toluenesulphonchloroamide — $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Na}\cdot\text{NCl}$ — "Chloramine-T," and p-toluenesulphondichloroamide — $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NCl}_2$ — "Dichloramine-T" were introduced by Dakin (1917) as general antiseptics and disinfectants. Their action is similar to that of the hypochlorites, and since they are stable, highly crystalline compounds, and readily soluble in water, it is highly probable that they will be found to be extremely useful antiseptics in the treatment of septic conditions of the mouth.

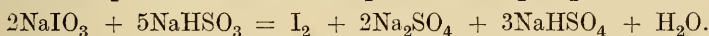
Iodine (I_2), is a member of the halogen group of elements, the other members of which are fluorine, chlorine, and bromine. It is obtained from sea-weed ash (kelp), which is first extracted with water so as to separate first the salts, *e.g.* potassium sulphate, potassium chloride, and sodium chloride, which are less soluble than the sodium iodide, which remains dissolved in the mother-liquor. This is mixed with manganese dioxide, and heated with sulphuric acid in iron pots, and the iodine which distils over is collected in a series of earthenware condensers,



Another method of obtaining the iodine is to precipitate it by passing in chlorine,



Iodine is also obtained from the sodium iodate ($NaIO_3$), which is found in the mother liquors obtained in the purification of a crude natural sodium nitrate (caliche). The sodium iodate is reduced by sodium bisulphite and the iodine separated after precipitation,



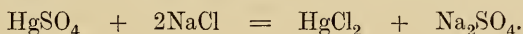
Crude iodine is readily purified by sublimation after mixing with potassium iodide in order to eliminate other halogens.

Iodine has an atomic weight of 126.92. It forms violet-black crystals, which have an almost metallic lustre. The melting-point of iodine is $113^\circ C.$, and although its boiling-point is as high as $184^\circ C.$, it has an appreciable vapour pressure at ordinary temperatures, and at the melting-point the vapour pressure is so high that iodine sublimates readily.

Although the solubility of iodine in water is small (about 1 in 5000), this straw-coloured aqueous solution is used as an antiseptic and astringent for syringing abscesses, etc. Iodine is much more soluble in alcohol, giving a brown solution, which is used in a strength of 2 per cent. for sterilising the gums before extractions and scalings. Iodine is much more soluble in aqueous solutions of potassium iodide than it is in water, and the brown solutions probably contain the unstable potassium periodide (KI_3). Solutions of iodine in aqueous solutions of potassium iodide are also used as counter-irritants, and also as antiseptics and astringents in dental surgery. The strength of the iodine solution used is $2\frac{1}{2}$ to 5 per cent. dissolved in a 10 per cent. aqueous solution of potassium iodide.

Mercuric Chloride, $HgCl_2$, corrosive sublimate, was introduced after phenol as a more powerful disinfectant, and undoubtedly it has a greater germicidal action in general surgical practice.

It is prepared by heating mercury in chlorine, or by distilling a mixture of mercuric sulphate with sodium chloride,



Mercuric chloride melts at 277°C . and boils at 303°C . It is a colourless, highly crystalline solid, which sublimes in needles. At 15°C . a saturated aqueous solution of mercuric chloride contains about 6.5 grams of mercuric chloride dissolved in 100 grams of water. Mercuric chloride is also soluble in ether, while its solubility in ethyl alcohol is almost five times as great as that in water. For the treatment of general septic conditions of the mouth the strength of the aqueous solution of mercuric chloride used is 1 in 2000 to 5000, and in spite of the excessively poisonous nature of the substance much stronger solutions either in water or in alcohol may be employed with care for special purposes.

Silver Nitrate, AgNO_3 , Lunar Caustic, is used not only as an antiseptic in mouth washes and in syringing abscesses, etc., but in the solid form is used as a caustic in the treatment of sensitive and carious dentine.

It is formed by dissolving silver in nitric acid, evaporating the solution to crystallisation, and then recrystallising the substance until free from acid. Silver nitrate forms characteristic transparent tabular crystals, which melt at 217°C .; the molten substance can be readily cast into sticks, and it is in this form that the substance is conveniently employed as a caustic.

The use of **zinc chloride** as an antiseptic, astringent, and caustic has been described elsewhere (p. 102),¹ and the remaining important dental antiseptics are organic compounds.

Formaldehyde ($\text{H}\cdot\text{CHO}$) is the direct oxidation product of methyl alcohol (CH_3OH),

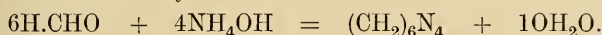


and this is the chief source. At ordinary temperatures it is a colourless gas, which condenses to a colourless liquid, boiling at -21°C . It has a characteristic pungent smell, and is highly soluble in water, and its 35 to 40 per cent. solution is known commercially as **formalin**. A solid polymerised form $(\text{H}\cdot\text{CHO})_3$, is known as trioxymethylene, which, at 180° to 200°C . volatilises, forming formaldehyde. Trioxymethylene is sold commercially in the form of pastilles for use in formaldehyde lamps for disinfecting rooms, etc.

In dentistry, formalin, suitably and largely diluted, is used as an antiseptic, as a mouth wash, for syringing septic pockets and abscesses, and for sterilising instruments. Undiluted formalin is used as a root dressing. As a germicide, formaldehyde appears to be quite as efficient as mercuric chloride, while its volatility gives it the additional advantage of being able to penetrate much more rapidly. **Hexamine** (urotropine, hexamethylenetetramine, cystamine) $(\text{CH}_2)_6\text{N}_4$,

¹ Crystalline copper sulphate, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, blue vitriol, is used to a small extent, more especially in the solid form as an antiseptic for root dressing.

which is an important urinary antiseptic, is formed by the action of ammonia on formaldehyde :—



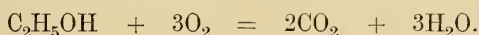
Hexamine owes its action to the liberation of formaldehyde, which occurs in acid fluids.

Ethyl Alcohol, $\text{C}_2\text{H}_5\text{OH}$, commonly referred to as alcohol, is the chief fermentation product of sugar, and is obtained by dehydrating the distilled fermentation products from sugar or indirectly from starch. Although the chemical reaction going on during the fermentation is frequently represented as :—



it is, in reality, much more complicated. The most probable reactions taking place have been elucidated by Harden and his co-workers.

When pure, ethyl alcohol is a colourless liquid boiling at 78.4°C ., and having a specific gravity at 20°C . of 0.8040 compared with water at 4°C . Pure ethyl alcohol is known technically as absolute alcohol. It is hygroscopic and mixes with water in all proportions, the mixing of the liquids being accompanied by an appreciable evolution of heat and a considerable contraction in volume. What is known as **proof spirit** contains 49 per cent. of alcohol by weight, or 57 per cent. by volume, and has a specific gravity of 0.920. Alcohol burns with an almost colourless flame, and the burning is accompanied by the production of a very large amount of heat. The products of combustion are water and carbon dioxide :—

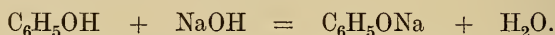


Pure, or absolute, alcohol is used in dental surgery for drying cavities and for deadening pain. Diluted with water to the extent of 1 in 20 it is used as a mouth wash, but, since ethyl alcohol possesses only a weak antiseptic action, its uses in dentistry are chiefly as a drier and as an obtundent.

Phenol, carbolic acid, $\text{C}_6\text{H}_5\text{OH}$ —the first of modern antiseptics to be introduced—when pure, is a colourless crystalline substance, melting at 42.5°C . and boiling at 181.5°C . It is an important product obtained in the distillation of coal tar, occurring in the carbolic oil fraction. This fraction also contains naphthalene, and after the latter has been crystallised out to a considerable extent, the oil remaining is treated with sodium hydroxide solution, which dissolves the phenol, forming sodium phenate, and leaves the accompanying basic substances unaffected. The sodium phenate solution, after concentration, is treated with sulphuric acid, when the phenol crystallises out on cooling.¹

¹ Phenol is also obtained from benzene. The benzene is first converted into its sulphonic acid, and the latter in the form of its sodium salt is fused with sodium hydroxide and the phenol extracted from the resulting alkaline liquid by means

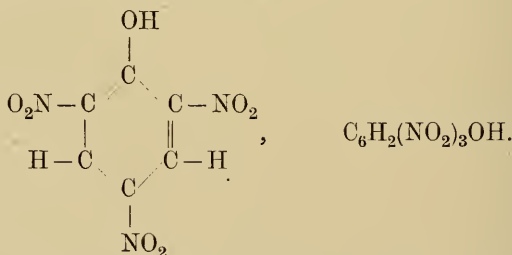
On exposure to air and light, phenol crystals assume a pink colour. Although phenol is sparingly soluble in cold water, the addition of a little water to phenol lowers the melting-point so much that the phenol liquefies. When phenol is shaken up with its own weight of water, two layers form; the upper layer consists of a solution of phenol in water containing about 7 per cent. of the former substance, while the lower layer is a solution of water in phenol containing about 7 per cent. of water. The acid nature of phenol is shown by the ease with which phenol dissolves in an aqueous solution of sodium hydroxide, whereby sodium phenate is formed:



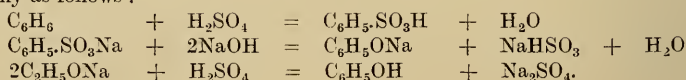
Phenol can be recognised by the characteristic smell and by its giving a violet coloration with ferric chloride. The latter property is, however, not characteristic of phenol, since other similar substances, *e.g.* the cresols (see below) also have a similar reaction. When bromine water is added to an aqueous solution of phenol, a white crystalline precipitate of tribromophenol, $\text{C}_6\text{H}_2\text{Br}_3\text{OH}$ (melting-point = $95^\circ \text{C}.$), is immediately produced. Further, when phenol is nitrated with dilute nitric acid, a mixture of ortho- and para-mononitrophenol is produced, and of these the para-compound is not

volatile in steam. Ortho-mononitrophenol, $\text{C}_6\text{H}_4 \begin{matrix} \text{OH}(1) \\ \text{NO}_2(2) \end{matrix}$, is a

yellow crystalline compound having a melting-point of $45^\circ \text{C}.$, and para-mononitrophenol crystallises from hot water in long colourless needles, which melt at $114^\circ \text{C}.$ When phenol or either of the nitrophenols is nitrated with concentrated nitric acid symmetrical **trinitrophenol** or **picric acid** is produced. The constitution of picric acid is usually represented by the formula:—



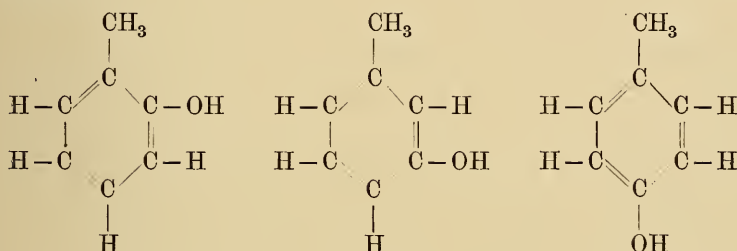
It crystallises from hot water or alcohol in yellow leaf-like crystals of sulphuric acid in the way already described. The reactions may be illustrated briefly as follows:—



or prisms which melt at 122.5° C. It is soluble in cold water to the extent of 1 part in 160, but it is much more readily soluble in hot water and in alcohol. It forms salts with bases, the metallic salts being easily exploded when subject to shock. The aqueous solution of picric acid is of great service as an application to the skin to prevent or minimise blistering after burns. It is also a mild antiseptic.

Phenol finds important applications in dental surgery. Its aqueous solutions are used in strengths varying from 1 part in 200 to 60 as mouth washes, whilst stronger solutions are used for sterilising instruments and for syringing septic portions of the mouth. Crystalline phenol is often a constituent of tooth powders, and 90 per cent. phenol is used as a caustic. 90 per cent. phenol is the *Ac. Carbolici Liq.* of the British Pharmacopœia.

Recently certain homologues of phenol have been used as antiseptics in place of phenol itself. Of these the most important are the three cresols or monohydroxytoluenes, $C_6H_4CH_3.OH$, ortho-, meta-, and para-cresol, having the following constitutional formulæ respectively,

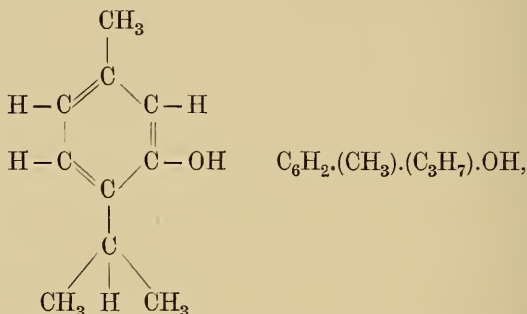


These three isomeric cresols all resemble phenol very closely in action. Metacresol is said to be less poisonous than phenol, and a more powerful antiseptic; orthocresol is described as being more dangerous than phenol, and paracresol as being the most dangerous of all (Cushny). Like phenol the cresols are constituents of coal tar, from which they can be separated in a similar manner to that employed in the separation of phenol. On account of their small solubility in water cresol preparations are usually employed in the form of emulsions with soap, etc., and **lysol** is an example of one of these. These emulsions appear to be more powerful antiseptics than phenol itself. According to Cushny, their insolubility in water facilitates their passage into the bacteria, in which they are more soluble; and the emulsion form has a further advantage since the fluid, coming in contact with the bacteria, must always be saturated with the antiseptic. In their chemical properties the cresols, being hydroxy derivatives of toluene, resemble very closely ordinary phenol, which is monohydroxybenzene.

Thymol is another phenol used as an antiseptic in dental surgery. Its solution in water, 1 part in 2000, is used as a mouth wash, but

a solution of this strength is a very weak antiseptic. A mixture of crystalline thymol with zinc oxide is used as an antiseptic root dressing.

Thymol is obtained by shaking oil of thyme (from *Thymus vulgaris*) with a solution of sodium or potassium hydroxide, and the filtered solution, after separating from the insoluble hydrocarbons (cymene, etc.), is precipitated with hydrochloric acid. Thymol is methylisopropylphenol, and its constitution may be represented by the formula,



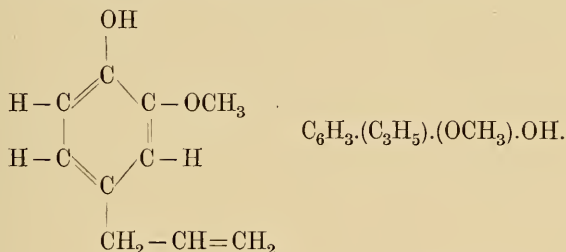
which indicates its close relationship to phenol and metacresol. Thymol crystallises in large colourless plates, which melt at 44° C., and boil at 230° C. The chief use of thymol is as an anthelmintic in the treatment of anchylostomiasis (hook-worm disease).

Before the introduction of the systematic application of antiseptics to wounded tissues by Lister in 1870 various balsams, tars, and aromatic substances had been long employed in the treatment of wounds of all kinds, and it is interesting to note that two essential or volatile oils, viz., **oil of cinnamon**, and, especially, **oil of cloves**, are still found extremely useful in dental surgery. Oil of cinnamon is used for the treatment of septic tooth cavities, and as a flavouring agent in tooth powders. Oil of cloves is used to relieve pain, and it also has a slight antiseptic action; the relief of pain is due to the oil, or one or more of the constituents, paralysing the exposed nerve ends after irritation.

The chief constituent of oil of cloves,¹ which is distilled from the flower buds of *Eugenia caryophyllata*, is eugenol. **Eugenol** is a phenol, and forms a potassium salt, corresponding to potassium phenate, on treatment with an aqueous solution of potassium hydroxide. The formation of this potassium salt and the liberation from it by treat-

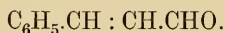
¹ Like all essential oils, oil of cloves and oil of cinnamon are complex mixtures containing a number of constituents. In addition to the eugenol, oil of cloves contains the sesquiterpene, caryophyllene ($\text{C}_{15}\text{H}_{24}$), methyl benzoate, methyl alcohol, etc. Oil of cinnamon contains the terpene, phellandrene ($\text{C}_{10}\text{H}_{16}$) in addition to cinnamic aldehyde and traces of eugenol.

ment with a mineral acid are made use of in extracting eugenol from oil of cloves. Eugenol is hydroxymethoxyallylbenzene, and its constitution may be represented by the formula,

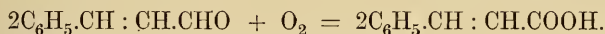


Eugenol is a colourless oil, boiling-point 244.5°C ., having the characteristic smell of cloves, and possessing a burning taste. It reddens litmus, and its alcoholic solution gives a blue colour with ferric chloride. Commercially, eugenol and oil of cloves are of importance for the production of vanillin.

The chief constituent of oil of cinnamon, obtained from the bark of *Cinnamomum Zeylanicum*, is **cinnamic aldehyde**, which has the constitutional formula,



Cinnamic aldehyde is a colourless liquid, boiling-point 247°C ., possessing the characteristic cinnamon odour. When exposed to air it is rapidly oxidised to the white crystalline cinnamic acid, melting-point 133°C .



Cinnamon oil also contains traces of eugenol.

CHAPTER XVII

RUBBER, VULCANITE, AND GUTTA-PERCHA

RUBBER AND VULCANITE

NATURAL rubber, or caoutchouc, is obtained from the latex of certain species of *euphorbiaceæ*, *apocynaceæ*, *urticaceæ*, and *compositæ*, but most of the plantation rubber is derived from *Hevea Brasiliensis*. The latex is a milk-like fluid which exudes in the process of "tapping" the tree or shrub, *i.e.* cutting through the outer bark and into the layer next to the cambium, in such a manner that the exuding latex can be conveniently collected. The latex consists of minute rubber drops or cells suspended in a watery fluid, and it is coagulated in different ways according to the district in which the rubber is produced. In the Amazon district it is coagulated by smoking over a fire made from *urucuri* nuts, while in the plantations it is usually coagulated by means of acetic acid. It may also be coagulated by sulphuric acid, hydrofluoric acid, or alcohol, or even by simple exposure to air. Other processes for the coagulation of the latex have also been devised, which depend on the fact that caoutchouc is a colloid the particles of which are negatively charged. After coagulation, the crude rubber is separated, if necessary, from the watery liquid, and may be passed through rollers to remove any adhering mother liquor, and dried by warm air. When the natural rubber contains foreign materials, such as woody fibre, sand, and other mechanical impurities, it is steeped in water, and passed between rollers rotating at different speeds, and, at the same time, washed with warm water. What is known as plantation rubber is usually imported in the form of sheets about half an inch thick, the appearance of which may vary from a translucent cream to dark amber colour.

Such natural rubber consists of caoutchouc or rubber, together with varying quantities of resinous substances (containing oxygen in varying proportions), mineral matter, proteid substances, etc. Well prepared natural rubber dissolves to the extent of 96 to 97 per cent. in solvents, such as benzene, solvent naphtha, carbon disulphide, chloroform, carbon tetrachloride, petroleum ether, turpentine, etc., and leaves from 3 to 4 per cent. of insoluble matter.

The essential constituent of natural rubber is known as caoutchouc or rubber proper, which is a hydrocarbon of high molecular weight, the composition of which is generally represented by the formula $(C_{10}H_{16})_n$. Although the actual constitution of the rubber molecule cannot be considered to have been finally determined,

it is clear that rubber bears a very close relationship to "gutta"—the essential constituent of gutta-percha—on the one hand (see p. 170), and probably to the naturally occurring terpenes, which are to a great extent isomeric hydrocarbons, having the formula, $C_{10}H_{16}$, on the other. The fact that rubber on distillation in absence of air yields a number of hydrocarbons, one of which is the unsaturated hydrocarbon, isoprene, C_5H_8 (β -methyl butadiene), whose constitution is known to be $CH_2=CH-C(CH_3)=CH_2$, and the fact that this hydrocarbon has been shown to undergo polymerisation, especially in the presence of sodium at $60^\circ C.$, to produce what is known as synthetic rubber, indicates, at least to some extent, the nature of the rubber molecule.¹ A large number of derivatives of natural and synthetic caoutchouc have been obtained by the action of ozone, oxygen, bromine, etc., on the parent substance or substances, and the study of such compounds is throwing additional light on the actual chemical composition of the rubber molecule.

Rubber is a colloidal gel having an organised structure which varies according to the mode of treatment. Rubber of good quality (*e.g.* Para rubber) has a density of 0.91. On warming, the density diminishes, the material softens, and finally melts at about $188^\circ C.$ At $0^\circ C.$ rubber becomes quite hard and loses its elasticity. Like most gels it absorbs water freely, increasing in weight and in volume to the extent of about 25 and 15 per cent. respectively. The solutions of rubber in organic solvents are extremely viscous.

The uses of natural rubber are comparatively few. Priestley, who discovered oxygen, mentioned its use for erasing pencil marks in 1770. It is a fairly good non-conductor of electricity, and is used as a wrapping for wires conveying an electric current; the wrapping is generally covered with an outer layer of vulcanised rubber. Natural rubber is adhesive, and it may be stated that but for the discovery of the process of vulcanisation, any extensive use of rubber in industry would have been impossible.

Although rubber had been used for a very long time for producing waterproof garments of various kinds, these were produced by a practicable process for the first time by Macintosh of Manchester. Macintosh's patent was taken out in 1823, and essentially consisted in dissolving rubber in naphtha and spreading the solution thinly on suitable

¹. Other unsaturated hydrocarbons, *e.g.* butadiene, $CH_2=CH-CH=CH_2$, have been shown to undergo polymerisation under similar conditions to produce rubber-like substances. Since such hydrocarbons can be produced comparatively readily, the manufacture of synthetic rubber might be a commercial possibility, see *Rubber*, by Schidrowitz (Methuen, 1916); *Recent Progress in Rubber Chemistry and Technology*, by Schidrowitz (Benn Brothers, Limited, 1922). Tilden, *Chemical News*, 1882, **45**, 120; Perkin, *Journal Society of Chemical Industry*, 1912, **31**, 616; Fernbach, *English Patents*, 15203 of June 29, 1911; 16925 of July 24, 1911; Harries, *Liebigs Annalen*, 1911, **383**, 157.

slabs so that the solvent could evaporate and leave a fairly homogeneous film of rubber which was then sewn on to the textile fabric. To overcome the drawback of the sticky nature of the surface so produced, Macintosh covered it with a second layer of fabric. The process, however, was far from satisfactory, and later, Hancock (1837) invented a spreading machine for impregnating the fabric with rubber itself. Up to this time ordinary natural rubber was employed, and on account of the properties of caoutchouc, articles containing it could not be free from obvious defects due to the physical properties of caoutchouc. It was not until the discovery of the process of the vulcanisation of rubber that satisfactory applications of rubber could be made.

Vulcanisation of Rubber

The process of vulcanisation of rubber was discovered by Charles Goodyear, of Newhaven, U.S.A., in 1839, and patented in 1844. His process for the production of soft vulcanite consisted in impregnating the natural rubber 25 parts with sulphur 5 parts, and white lead 7 parts, and heating the mixture. Hancock about the same time found that the same effect could be produced by dipping the natural rubber into molten sulphur. Such "cured" or vulcanised rubber, unlike the natural rubber, was not dissolved by the ordinary organic solvents, and its properties were not altered by cold or by heat so long as the temperature did not rise above the temperature of vulcanisation. This process of vulcanisation may be described as the "hot process" in contradistinction to the "cold process" of vulcanisation patented by Parkes in 1846. Parkes' cold process consisted in subjecting thin layers of natural rubber, or fabrics impregnated with rubber, to the action of a solution of sulphur monochloride (S_2Cl_2) in carbon disulphide. This latter process has been modified from time to time, but most of the modern processes of "curing" rubber-impregnated fabrics are based on it.¹

¹ An ingenious process for the "cold curing," or cold vulcanising, of rubber which produces a soft vulcanite is that recently patented by Peachey (Brit. Patent No. 129826, of 1918, and described also in *Rubber Age*, 1922, p. 63). The Peachey process consists essentially in exposing the rubber, or the rubber-impregnated fabric, to the action of sulphur dioxide for about 10 minutes in a chamber constructed of aluminium, when the gas is absorbed. The article to be "cured" is next submitted, after the chamber has been swept out by a current of air, to the action of hydrogen sulphide for about 30 minutes, when the following reaction



takes place within the rubber itself, and the sulphur, liberated in a highly active form, then vulcanises the rubber immediately. This possesses many advantages over the other processes for the "curing" of rubber. It can be applied to rubber-impregnated fabrics which have been dyed with the large number of organic dye-stuffs which are not affected by either of the above gases. It is carried out at the ordinary temperature, and lends itself to the production of a large number of highly

For making hard rubber, or what is generally termed "vulcanite," Nelson Goodyear patented a process in 1851 which consisted in heating to a suitable temperature an impregnated mixture of 1 part of sulphur, 2 parts of natural rubber or caoutchouc, and 1 part by weight of a number of inorganic substances. On this was based the patent (1851) of Charles Goodyear, Junior, "For improvement in plates for artificial teeth." This process consisted in heating a thoroughly impregnated mixture containing 1 part by weight of sulphur and 2 parts of natural rubber or caoutchouc together with a suitable colouring substance such as vermilion (mercuric sulphide, HgS) or iron oxide. The colouring substance was mixed with zinc oxide to produce varieties of shade, and it was pointed out that what are now described as "filling materials" must be capable of withstanding the temperature of vulcanisation. The impregnated mixture was gradually heated during six hours to a temperature of 110°C ., and then finally for a short time to 146°C .

In dental practice, rubber is always vulcanised by the hot process, and the degree of hardness of the vulcanite produced is varied by altering the sulphur content of the mixture, keeping the other conditions, temperature, and time of vulcanisation the same.

Regarding the composition of the mixture for producing vulcanite for artificial dentures, the following are given by Professor Wildman, and quoted by Wilson ¹ :—

Dark Brown

Caoutchouc	66.66 per cent.
Sulphur	33.33 " "

Red

Caoutchouc	44.44 " "
Sulphur	22.22 " "
Vermilion	33.33 " "

Dark Pink

Caoutchouc	42.76 " "
Sulphur	21.38 " "
Zinc Oxide	26.78 " "
Vermilion	8.90 " "

artistic and useful fabrics, many of which are unobtainable by the use of other vulcanising processes. Further, the process is applicable not only to rubber in its usual state, but can also be applied to rubber in solution, and therefore the production of moulded articles made of rubber is possible by this process.

It is highly probable that the scientific investigation of the Peachey process now in rapid progress will afford valuable information regarding the chemistry of vulcanisation.

¹ *Dental Prosthetics, loc. cit.* p. 197.

Grayish White

Caoutchouc	28.57	per cent.
Sulphur	14.28	„ „
Zinc Oxide	57.14	„ „

Black

Caoutchouc	50.0	„ „
Sulphur	25.0	„ „
Ivory black or drop black	25.0	„ „

Jet Black

Caoutchouc	40.0	„ „
Sulphur	20.0	„ „
Ivory black or drop black	40.0	„ „

It will be noticed that the above mixtures contain the caoutchouc and sulphur in the proportion of 2 to 1 by weight, the original proportions recommended in the above patent. It is highly probable that the impregnated mixtures supplied by the manufacturers may differ in composition from the above to a greater or less extent. For producing the typical soft vulcanite, popularly known as "velum rubber," 1 part by weight of sulphur should be impregnated with 5 parts of natural rubber or caoutchouc.

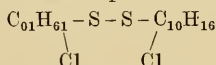
The temperature of vulcanisation for producing dental vulcanite is 160° C. (320° F.), and this is conveniently attained by carrying out the vulcanisation in the vulcaniser in which water is heated under pressure (90 pounds per square inch). The temperature under normal circumstances should remain at 160° C. for about fifty-five minutes, after which vulcanisation is complete, and the vulcaniser and its contents can be allowed to cool.

In all probability vulcanisation of rubber is a chemical reaction which consists in the formation of an addition compound (or compounds) by the caoutchouc molecule with sulphur. The caoutchouc molecule being unsaturated, the formation of an addition product (or products) is easily understood. It has been stated (Weber) that a series of such sulphur addition compounds, varying in composition from $(C_{10}H_{16})_{10}S$ to $C_{10}H_{16}S_2$, probably results from the vulcanisation process according to the conditions and the reacting quantities, and that the hardness of the compounds produced increases with increasing sulphur content. It should be pointed out, however, that other explanations of the vulcanisation process have been put forward, and that, whilst the formation of chemical compounds explains most of the observed facts, our knowledge of the process is at present by no means complete. If vulcanisation consists in the formation of addition compounds of sulphur to the caoutchouc molecule, it is clear that no hydrogen sulphide should result from the reaction, otherwise

substitution is indicated. It has been asserted that no hydrogen sulphide is produced when vulcanisation is carried out under the proper conditions, and if hydrogen sulphide is produced it is generally taken as a sign that something has gone wrong. It rarely happens, however, that hydrogen sulphide is not produced, but since it is never produced in anything like the quantity that it would be if substitution of sulphur for hydrogen in the caoutchouc molecule took place to any appreciable extent, its production in normal cases is probably due to some unexplained reaction between the sulphur and the other substances in the natural rubber, and not the caoutchouc itself.¹

Advantages and Disadvantages of the Use of Vulcanite for Denture Plates.—After the process of vulcanisation, as carried out properly in the dental laboratory, is completed, the resulting material is very little affected by the usual organic liquids which dissolve caoutchouc, and it is completely unaffected by oral fluids. It is not adhesive, very strong, tough, highly elastic, and capable of being highly polished. Since vulcanised rubber becomes soft at the temperature of vulcanisation, a broken vulcanite plate can be easily repaired. The density of hard dental vulcanite depends to a considerable extent on the nature and relative quantity of the filling materials, and it varies from about 1.15 to about 1.75. It is the lightest of all materials used for denture plates, being considerably lighter than aluminium, the lightest of all metals employed for the same purpose. Apart from its being inexpensive, a vulcanite plate is easily made, and no material is so useful for restoration work and for adapting to contours of all kinds. The properties and appearance of vulcanite can be varied considerably by using different filling materials. Apart from those

¹ It has been suggested that in the sulphur monochloride "cold" vulcanising process, which can only be employed to thin rubber goods, the end product is an addition compound of caoutchouc and sulphur monochloride, having the formula :



As in the case of the "hot" vulcanisation process, the formation of definite compounds has not yet been finally established, and authorities on the subject still hold widely different views. Whether produced by a "cold" or a "hot" process, vulcanisation is very difficult to investigate from a chemical standpoint, chiefly on account of dealing with such a complex substance as caoutchouc. It seems clear that vulcanite, whether hard or soft, cannot be a simple substance, and while compounds of caoutchouc with sulphur monochloride or sulphur may be contained in it, these compounds may be in a state of solid solution with sulphur or caoutchouc, or the excess sulphur may be "absorbed" by the colloid caoutchouc.

No mention has been made in the present brief account of the use of accelerators for the vulcanisation process. These are, generally speaking, weakly basic substances, and both inorganic and organic substances have been used for this purpose.

Recent Progress in Rubber Chemistry and Technology, loc. cit. p. 36 et seq., contains a good account of inorganic and organic accelerators, and the author (Schidrowitz) also gives references to the more important literature on the subject.

mentioned above, aluminium is frequently employed for this purpose. In vulcanising a thick piece of rubber, pieces of aluminium foil dropped into the rubber impregnated with the usual substances has been shown to facilitate even vulcanisation, and improve the quality of the vulcanite without increasing its weight unduly. Aluminium, in the form of powder, impregnated into the rubber mixture produces, after vulcanisation, a vulcanite with a beautifully lustrous metallic surface. The vulcanite produced from this so-called "Golddust" rubber is claimed to have superior properties as a denture material to those of ordinary vulcanite.

On the other hand, the use of vulcanite is attended by certain disadvantages. It is such a poor conductor of heat that the constant wearing of a vulcanite plate in the mouth causes a lowering of the vitality of the soft tissues and an excessive resorption of the hard tissues. Another very great drawback to hard vulcanite for denture plates is, that in the making the ultimate contraction of the material is very appreciable. It is a matter of experience that the greater the relative quantity of filling material, the less contraction takes place during vulcanisation, but so far, the contraction that occurs has not been anything like adequately prevented. It is true that the contraction can be controlled to some extent by carrying out the vulcanisation in the minimum time and between thin tin foil, which, on account of the pressure, minimizes the contraction of the vulcanite away from the model. Unfortunately, it must be recognised, however, that the problem of preventing the contraction in making a vulcanite denture plate has still to be solved, and the difficulty caused by the contraction has also to be dealt with whenever a vulcanite denture plate has to be repaired.

GUTTA-PERCHA

Gutta-Percha is the inspissated latex obtained from incisions made through the bark of trees belonging to the order *Sapotaceæ*, which are indigenous in the Malay Peninsular and Archipelago. The name is derived from "getah," gum, and "percha," name of the tree (Malay). The essential constituent of gutta-percha is a hydrocarbon, **gutta**, having the formula $(C_{10}H_{16})_n$, and this is associated with certain resinous substances which are complex mixtures, probably oxidation products of "gutta" itself. It will be seen that gutta-percha resembles rubber (see p. 165) in that the essential constituent of both is a hydrocarbon having the same empirical formula, and evidence¹ has been brought forward to show that the hydrocarbons of gutta-percha and rubber are identical.

¹ Harries, *Ber. der Deutschen Chemischen Gesellschaft*, 1905, **38**, 3985.

Ramsay, Chick & Collingridge, *Jour. Society of Chemical Industry*, 1902, **21**, 1367.

Caspari, *ibid*, 1905, **24**, 1274.

Crude gutta-percha varies greatly in colour from dark brown to whitish-yellow, and the amount and quality of the yield depends on the particular tree, its condition, and the time of tapping. The amount of gutta in different samples varies from about 11 to 50 per cent., and foreign matter (dirt and moisture), makes up the remainder. To purify the crude gutta-percha, the blocks as imported are cut into slices by machinery, washed in hot water, and when soft enough the masses are passed through a machine which shreds them. The shredded material is again washed in water, when the heavier foreign particles sink to the bottom of the trough, whilst the lighter gutta-percha floats, and is removed. It is next heated by steam and worked up, while soft, into blocks of suitable size. Purification, as complete as possible, is important, otherwise the material oxidises and deteriorates fairly rapidly.

At ordinary temperatures gutta-percha is hard, tenacious, and, unlike rubber, cannot be stretched. On immersion in hot water it becomes soft and plastic, and can be easily moulded. On cooling, it again becomes hard, and retains the shape given to it when soft. The odour of burning gutta-percha is very like that of burning rubber, and when gutta-percha is distilled in absence of air it is decomposed into a mixture of hydrocarbons, including isoprene, which is also produced from rubber under similar conditions.

Gutta-percha is not only insoluble in water, but it is unattacked by dilute mineral acids, by acetic acid, and even by strong hydrochloric acid. Concentrated nitric and sulphuric acids act upon it very readily. It is only partly soluble in ether, acetone, alcohol, and cold petroleum ether, when the resin is chiefly dissolved. It is completely dissolved by chloroform, carbon tetrachloride, and carbon disulphide.

The hydrocarbon, gutta, the essential constituent of gutta-percha, possesses the essential properties of gutta-percha of good quality, and towards chemical reagents acts in a similar manner to caoutchouc, the essential constituent of rubber.

Gutta-percha is used in dental practice as a filling material, for taking impressions,¹ as a soft lining for lower dentures, and for setting

¹ The use of plaster of Paris for taking impressions has already been discussed. The use of gutta-percha as an impression material has been largely superseded by the use of suitable waxes, such as good quality bees wax, and especially by what are known as "modelling compounds." These are generally complex mixtures of such substances as dammar resin (often inaccurately described as "gum dammar"), stearin, and French chalk, together with suitable colouring matters and flavouring materials. These modelling compounds are softened by heating in hot water, and possess a certain amount of elasticity when cold. To secure the advantage of this property in the reproduction of undercuts, it is necessary to remove the impression from the mouth at the right moment, *i.e.* at a point when the compound has become moderately hard, yet not too hard as to require great force to remove it from deep undercuts, otherwise the body of the impression may become distorted by the force employed. For an account of modelling compounds in general use, consult Wilson's *Dental Prosthetics*, *loc. cit.* pp. 66-68.

crowns and bridges. For these various purposes, other substances are added with the object of imparting special properties, *e.g.* hardness, colour, flavour, etc., to the gutta-percha.

As a filling material gutta-percha possesses certain qualities which render it highly useful. When softened, it is easily inserted; it is a very poor conductor of thermal changes; it is compatible with the tooth substance; it is insoluble in the oral fluids, and it protects the tooth against recurrent caries. The chief disadvantage is that it is liable to be subjected to much mechanical stress, causing distortion during mastication. It is also often porous, and tends to become foul after being in use for some time. The wearing qualities of gutta-percha are greatly improved by thoroughly impregnating with it such substances as zinc oxide and the finest silica. Pink gutta-percha for base plates contains vermilion in addition to zinc oxide.

To prevent its deterioration (probably due to oxidation) gutta-percha should be kept away from the light and stored in receptacles as nearly air-tight as possible. In softening, overheating should be avoided, as gutta-percha is easily inflammable and oxidised. Gutta-percha may be conveniently softened by placing it on a slab of mica or soapstone, which is heated by means of a spirit flame. This will prevent any actual contact with the flame.

Gutta-percha for temporary fillings is impregnated with white paraffin wax, Burgundy pitch (the resin of *Picea excelsa*), zinc oxide, chalk, and usually some colouring matter. It is extremely useful for sealing medicaments in a tooth cavity, for preserving and promoting space between adjacent teeth preparatory to filling, and for filling root canals. It softens more easily and at a much lower temperature than the gutta-percha mixtures employed for more permanent purposes, it is more easily inserted and removed, and is somewhat adhesive. It is quickly worn away by attrition, and its porosity is a drawback to its prolonged use.

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